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HISTORICAL PAPERS ON MODERN EXPLOSIVES

BY

George W. MacDonald, M.Sc. (Melb.)

(HEAD OF RESEARCH, MESSRS CURTIS'S & HARVEY, LTD.

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WITH AN INTRODUCTION BY

Sir Andrew Noble, Bart., K.C.B., F.R.S.

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DEDICATED TO

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(PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF MELBOURNE)

BY

ONE OF HIS STUDENTS

P R E F A C E

THE papers in this volume have appeared at intervals during the last few years in the pages of *Arms and Explosives*. I am indebted to Mr MAX BAKER, the editor of that journal, for his courteous permission to republish them in a collected form. The earliest literature of modern explosives is, in many cases, not readily accessible, and it often contains observations and experiments which are generally considered to be the results of much later investigation. The unevenness of style in the various papers may be criticized, and I would, therefore, like to point out that the original composition has been followed as closely as possible. Abel's work, extending as it does over 110 pages of the *Philosophical Transactions of the Royal Society*, has, of necessity, been greatly compressed, and I have, for convenience of reference, grouped it under various headings, and in many cases reduced tabulated results to statements of fact. The title of the book covers a much wider field than has actually been dealt with, but I hope that these papers may serve as a useful reference to some of the pioneer work upon which the vast industry of modern explosives has been erected. My thanks are due to Mr E. R. CRYSTALL, B.Sc., F.I.C., and Mr E. B. ADAMS, B.Sc., for reading the proof, and I am further indebted to the former for preparing the Index.

G. W. M^{OD}.

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INTRODUCTION

THE historical papers contained in this volume by Mr. G. W. MacDonald are an invaluable contribution to the history of the wonderful advance that has been made in explosives during the latter half of the nineteenth century.

Gunpowder, which, for so many centuries, held its place as the sole explosive and propellant, had during these centuries and till the middle of last century but trifling alterations as regards composition, and but little or no attention paid to density or size of grain.

More singular, however, were the extraordinary differences of opinion as regards the pressure developed by explosion. Robins (in 1742) considered the pressure when the space was completely filled (that is at a density of unity) to be about 1000 atmospheres, or 7 tons on the square inch, while Count Rumford, whose experiments gave variable results, placed the tension at about 100,000 atmospheres, or 660 tons on the square inch.

Rumford's higher estimate does not seem to have been accepted, but even so late as 1870 Piobert fixed the probable pressure at about 150 tons on the square inch, Cavalli at 158 tons, while the *Text-Book of the R.M. Academy, Woolwich*, placed it at 14·4 tons per square inch.

The researches communicated to the Royal Society in 1874, gave the pressures at all densities up to unity, that at unity being about 42 tons on the square inch.

The manufacture of gunpowder after the date named was very greatly improved, very much higher velocities being obtained concurrently with lower pressures.

On the introduction of guncotton and other modern propellents, careful experiments have been made, both in regard to their stored-up energies and also to their keeping qualities.

• Mr MacDonald's work will be invaluable to all interested in explosives.

A. NOBLE.

HISTORICAL PAPERS ON MODERN EXPLOSIVES

CHAPTER I

HOWARD'S DISCOVERY OF FULMINATE OF MERCURY (1800)

THE mercurial preparations which, when mixed with sulphur, fulminate on gradually exposing to a gentle heat were discovered by Bayen at the end of the eighteenth century. In 1800, Edward Howard communicated to the Royal Society a paper ¹ "*On a New Fulminating Mercury.*" After quoting the work of Bayen he states that mercury and most, if not all of its oxides, may, by treatment with nitric acid and alcohol, be converted into a whitish crystallized powder possessing all the inflammable properties of gunpowder as well as many peculiar to itself. He was led to this discovery by the assertion that hydrogen was the basis of muriatic acid. It induced him to attempt to combine different substances with hydrogen and oxygen.

With this view he mixed such substances with alcohol and nitric acid, as he thought might, by predisposing affinity, favour, as well as attract an acid combination of the hydrogen of the one to the oxygen of the other. The pure red oxide of mercury appeared suitable for this purpose. It was, therefore, intermixed with alcohol, and upon both nitric acid was affused. The acid did not act upon the alcohol so immediately as when these fluids are alone mixed together, but first gradually dissolved the oxide. After some minutes had elapsed a smell of ether was perceptible and a white dense smoke was emitted with ebullition. A dark-coloured precipitate was thrown down which, by degrees, became nearly white. The precipitate was separated by filtration and consisted of small acicular crystals having a saline taste. Finding that a part of the

mercury was volatilized in the white fumes, Howard states that he was not altogether without hope that muriatic acid had been formed, and united to the oxide of mercury. He, therefore, for obvious reasons, poured sulphuric acid upon the dry crystalline mass. A violent effervescence ensued, and, to his great astonishment, an explosion took place. The singularity of this explosion induced him to repeat the process several times, and, finding that he always obtained the same kind of powder, he prepared a considerable quantity of it. He gives the following method as the most satisfactory for the preparation of fulminate of mercury:—One hundred grains of mercury are dissolved, by heating, in $1\frac{1}{2}$ drams of nitric acid (sp. gr. 1·3). This solution is poured cold upon two ounces of alcohol (sp. gr. 0·849) contained in a glass vessel. Moderate heat is applied until effervescence takes place. The precipitate is collected on a filter, washed with distilled water, and dried at a temperature not exceeding that of the water bath. It was noted that fulminate varied in colour, and Howard states that his yield was from 120 to 132 grains of fulminate from one hundred grains of mercury. He once poured six drams of concentrated sulphuric acid on fifty grains of fulminate. An explosion took place, almost at the instant of contact. He states that he was wounded severely and most of his apparatus was destroyed, and then adds, “I must confess I feel more disposed to prosecute other chemical subjects.” The following account is given by Howard of experiments which he carried out:—Nitric acid acts upon fulminate, giving nitrous gas, carbon dioxide, acetic acid, and forming nitrate of mercury. On treating fulminate with dilute sulphuric acid it was found that oxalate of mercury was produced. Fifty grains of fulminating mercury when treated with three drams of sulphuric acid, diluted with water, gave, on heating, 28 to 31 cubic inches of gas, which left, after absorbing the carbon dioxide by ammonia solution, five to seven cubic inches of inflammable gas burning with a greenish-blue flame. One hundred grains of the powder were found to contain 64·72 grains of mercury. When three to four grains of fulminate were placed on a cold anvil and struck with a cold hammer, Howard states that a very stunning disagreeable noise was produced and the faces of the hammer and anvil were much indented. The shock of an electric battery produced a similar

shock generally acted on the fulminate like the blow of a hammer. When two or three grains of fulminate in a capsule of leaf tin were floated on heated oil it was found that it exploded at a temperature of 368° F. A gunpowder proof barrel holding eleven grains of fine gunpowder was filled with fulminate, and fired with a flint and steel. The report was sharp but not loud. The person who held the proof barrel in his hand felt no recoil, but the explosion laid open the upper part of the barrel nearly from touch-hole to muzzle, and struck off the hand of the register. A gun holding 68 grains of gunpowder was charged with 34 grains of fulminate and fired from the shoulder. The breech was torn open, the touch-hole driven out and the barrel split. Two blocks of wood of the same size were bored to the same depth. One was charged with half an ounce of best Dartford gunpowder; the other with half an ounce of fulminate. Both blocks of wood were buried in sand and the explosives were fired by a train. The block containing the gunpowder simply burst into three pieces, and had its parts fairly separated. That charged with fulminate burst in every direction and the parts immediately contiguous to the fulminate were absolutely powdered. Yet the whole hung together; in short, fulminate acted with the greatest energy, but only within certain limits. A mixture of coarse and fine grain gunpowder was spread on a quantity of fulminate. After inflammation of the latter, most, if not all of the grains of gunpowder were collected. Howard asks if this extraordinary fact could not be explained by the rapidity of combustion of the fulminate. He also suggests that, as gunpowder did not explode at the temperature at which mercury was volatilized, it might be considered that sufficient heat was not developed during the decomposition of the fulminate to inflame the gunpowder. Ten grains of fulminate were placed in a glass globe seven inches in diameter and half an inch thick. The fulminate was fired electrically and produced four cubic inches of gas which was proved to contain nitrogen and carbon dioxide. Attempts were made to produce, with alcohol, fulminating compounds from gold, platinum, antimony, tin, copper, iron, lead, nickel, bismuth, cobalt, arsenic, and manganese. Silver, alone, produced a small quantity of a fulminating compound. On the instructions of Lord Howe, Lieutenant-General of Ordnance, Howard carried

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Woolwich on the bursting of cast-iron cases filled with fulminate. Howard's conclusions may, in his own words, be summed up as follows:—"The effects of gunpowder and fulminating mercury admit of little comparison. The one exerts, within limits, an almost inconceivable force. The agents seem to be gas and caloric, very suddenly set at liberty, and both mercury and water thrown into vapour. The other displays a more extended, but inferior, power. Gas and caloric are, comparatively speaking, liberated by degrees, and water is thrown into vapour. Hence it seems that fulminate of mercury can seldom, if ever, be applied to mining, and, from the immensity of its initial force, cannot be used in firearms, unless in cases where it becomes the object to destroy them. The operation by which the powder is prepared is, perhaps, one of the most beautiful and surprising in chemistry. The superabundant nitrous acid of the mercurial solution must first act on the alcohol and generate ether, nitrous etherized gas and oxalic acid. The mercury unites to the last two in their nascent state, and relinquishes fresh nitrous acid to act upon an unaltered alcohol. The oxalic acid, although a predisposing affinity seems exerted in favour of its quantity, is evidently not formed fast enough to retain all the mercury; otherwise, no white fumes, during a considerable period of the operation, but fulminating mercury alone, would be produced."

CHAPTER II

BRACONNOT'S DISCOVERY OF NITROSTARCH (1833)

THE discovery in 1833 by Braconnot,¹ Professor of Chemistry in Nancy, of nitrostarch or *xyloiline* as he called it, and the subsequent work by Pelouze² on the same subject, are a very interesting prelude to Schönbein's discovery of guncotton in 1846. Immediately after Schönbein's announcement, Pelouze put forward certain claims in the French Academy as regarded the question of priority—claims which Schönbein promptly refuted. In order to allow a clearer understanding of the historical aspect of the question, and of the state of knowledge of the time, the communications of Braconnot and Pelouze are quoted in full in the remainder of the paper.

Braconnot wrote as follows:—

It is well known that dilute nitric acid dissolves potato starch producing a gummy liquid very soluble in water. Quite different results, however, are obtained with concentrated nitric acid. The author has treated 5 grms. of starch with a considerable quantity of concentrated nitric acid with continuous agitation. A thick transparent liquid was obtained. This liquid when poured into water throws down a copious, white, curdy precipitate, which, when well washed and dried, weighed exactly 5 grms. It is white, pulverulent, tasteless, and does not redden blue litmus paper. It is coloured brown by a solution of iodine. Bromine, on the other hand, has no action upon it. On boiling with water it is not dissolved, but unites together into a mass. It is not attacked or dissolved by dilute sulphuric acid. Concentrated sulphuric acid produces a clear solution of a gummy nature, which is not precipitated by water. Concentrated hydrochloric acid dissolves it readily, especially when heated. The addition of water throws down the original material again, in an unchanged condition. Of all the vegetable acids, acetic acid, alone, reacts with it. It is readily soluble, especially on heating, and so much can be got into solution

¹ *Annales de Chem. et Phys.* (1833).

² *Comptes Rendus* (1838), 713.

that the liquid becomes gummy in consistency. In contact with water a white, hard, thick coagulated precipitate is produced. On drying at a low heat a transparent material is obtained, which retains its transparency when placed in water. This thick acid liquid when applied to paper or other materials leaves a very brilliant varnish-like coating, superior to that furnished by the best gums, whilst, at the same time, it is perfectly impervious to water. Linen, coated with this material, retains its impermeability even on boiling with water. These properties show the advantages this material is able to offer in the arts. Boiling wood vinegar dissolves it, and a slight precipitate is thrown down on cooling. Neither ammonia nor caustic potash dissolves it, but they convert it into a transparent body. On boiling a brown solution is obtained, and by neutralization a precipitate is produced but slightly differing from the original material. It is softened by boiling water without being dissolved, and acquires, by drying, the transparency of a gum. On exposing this material to heat it ignites with great readiness. It suffices even to heat it upon a piece of thick paper to produce rapid carbonization and liquefaction, whilst the cardboard itself, exposed to the heat, is not sensibly damaged. Heated in a small glass retort, it leaves a residue of one-sixth of its weight of carbon, difficult to incinerate, and gives a brownish liquid distillate containing much acetic acid. In contact with a solution of indigo sulphate, largely diluted with water, it is not sensibly coloured blue and does not decolourize the solution. It does not show any indication of reacting with ferrous sulphate. As this material appears, in some respects, to resemble lignin, the author proposes for it the name of *Xyloidine*. Several other vegetable substances are acted on in a similar manner by the addition of nitric acid. The following observations were made on the action of concentrated acid upon lignin and gummy materials. Sawdust, when acted on by nitric acid, swells up without dissolving. On exposing the mixture to a certain temperature there is no sign of effervescence, which is very remarkable. A gummy solution is obtained so thick that it solidifies on cooling. The addition of water separates abundantly a material precisely similar to that obtained by the action of concentrated nitric acid on starch. Cotton and linen warmed with the same acid are partially dissolved, without any sensible reaction, and are

converted into xyloïdine. Sugar cane, mannite and milk sugar produce nothing, except, in the case of the sugars, a very bitter material. Gum tragacanth, gum arabic, inulin as well as saponin, which the author has discovered in the bark of *gymnocladus canadensis*, are, by the action of nitric acid, converted into xyloïdine. It is true that it is accompanied by a very bitter material from which we may conclude that these gummy materials contain sugar in some form.

In 1838 Pelouze communicated the following results:—

Braconnot noticed, some years ago, that concentrated nitric acid completely altered several substances, notably starch and wood fibre, into quite a new material, which he called xyloïdine. He mixed starch with several times its own weight of nitric acid. When the starch was quite dissolved in the acid, he added water, which immediately separated the xyloïdine in the form of a white, insoluble precipitate, which upon washing and drying, was found to be quite pure. The composition of this substance and the various circumstances which accompany its formation have not been examined. The chief properties have been either imperfectly determined or are completely unknown. My paper will, I hope, make xyloïdine better known, and call the attention of chemists to these interesting points about the chemistry of starch. If you make a mixture of starch and concentrated nitric acid of a sp. gr. of 1.5, the starch will have completely disappeared at the end of several minutes. The liquid will still retain the pale yellow colour of concentrated nitric acid and no gas is given off. If water is added immediately, xyloïdine will be completely precipitated, and the filtrate, when evaporated, leaves practically no residue. If, instead of adding water immediately the starch is dissolved in the nitric acid, the solution is left in a closed jar, it changes colour by degrees, and takes the colour of a mixture of nitric acid and oxides of nitrogen. If water is then added, the precipitate of xyloïdine will be found to have greatly diminished. In fact at the end of two days (sometimes even of several hours) no precipitate will be found. The xyloïdine has been entirely destroyed and a completely new acid is formed, which upon evaporation is found in the form of a solid, white, non-crystalline deliquescent mass, the weight of which is considerably heavier than the starch taken for the experiment. Neither carbonic acid nor oxalic acid is produced during the

reaction. Xyloïdine, the product first produced by the action of nitric acid on starch, is a compound of these two bodies. It may be considered as starch in which a molecule of water has been replaced by a molecule of nitric acid. Starch is completely converted into this body, a fact which explains the considerable increase of weight observed when starch, after being dissolved in nitric acid, is immediately precipitated by water. As an excess of nitric acid converts xyloïdine into a very soluble compound, identical with the new acid which I have previously described, it can be readily understood why Braconnot obtained different results. Braconnot obtained from a given weight of starch the same weight of xyloïdine. It is therefore evident that part of the xyloïdine has been already decomposed as previously described. In fact, should the precipitation of the solution by water not take place till after the lapse of some time, no trace of xyloïdine is obtained. If a mixture of starch and concentrated nitric acid is heated to boiling point, the starch is decomposed in the course of a few minutes and converted into a deliquescent acid which can be obtained in a pure condition by evaporation on the water bath. This acid is the same as I have previously described and contains no nitrogen. It has some points of resemblance to nitro-saccharic acid, but has a different composition. At a moderate heat it is converted into another acid, dark in colour, soluble in water, and converted by nitric acid into the original compound from which it was derived. Concentrated boiling nitric acid only attacks it with difficulty. Nitric acid in the cold converts it gradually into oxalic acid, without production of any carbonic acid. We thus see that starch is converted by the action of nitric acid successively into xyloïdine, a deliquescent acid, and oxalic acid, without any displacement of the carbon atoms in the compound. I have already remarked, that xyloïdine results from a combination of starch with the elements of nitric acid, producing a compound in which starch may be considered as taking the part of a base. Xyloïdine is extremely combustible, and at a temperature of 180° C. it ignites and burns with very considerable violence, leaving practically no residue. This property has led me to make certain experiments which, I believe, may be of some practical application, particularly in the case of artillery. On dipping paper into nitric acid of a specific gravity of 1.5, allowing sufficient time for the acid to

penetrate the paper (two or three minutes is generally sufficient), removing the paper, and washing with a large volume of water, a parchment-like material is obtained, impermeable to moisture, and of extreme combustibility. The same compound is obtained on using linen and cotton fabrics. Paper and fabrics which have thus been submitted to the action of nitric acid owe their new properties to the xyloïdine which covers them.

CHAPTER III

SCHÖNBEIN'S DISCOVERY OF GUNCOTTON (1846)

CHRISTIAN FREDERICK SCHÖNBEIN, the discoverer of guncotton, was born on 18th October 1799 at Metzingen, Wurtemberg, and died on 29th August 1868 at Sautersberg near Baden-Baden. He was Professor of Chemistry at Bâle, and announced his discovery of guncotton on 27th May 1846, at a meeting of the Society of Scientific Research at Bâle.

The steps leading up to the discovery, as well as the attitude taken up by Schönbein to certain claims made by Pelouze in the French Academy, as regards priority, may be best appreciated by quoting Schönbein himself.¹

"The substance to which I have given in Germany the name *Schiesswolle*, and in English that of guncotton, having excited a lively curiosity, it may be interesting to the scientific world to become acquainted with some details of the way in which I was first led to its discovery. The results of my researches on ozone led me, in the last few years, to turn my attention particularly to the oxides of nitrogen and principally to nitric acid. The numerous experiments which I have made on this subject have led me, as I have stated in detail in *Poggendorff's Annalen*, to adopt a peculiar hypothesis of the so-called hydrates of nitric acid, sulphuric acid, etc., as well as the normal nitrates, sulphates, etc. For a long time I have entertained doubts as to the existence of compound bodies of this nature, which cannot be isolated, and which are stated to be capable of existing only in combination with certain other substances. For a long time, also, I had come to the conclusion that the introduction of these imaginary combinations had only been an apparent progress in theoretical chemistry, and that it had even impeded its development. It is well known that what has most contributed to the admission of the existence of these compounds has been the opinion, generally received among chemists, respecting the nature of nitric acid. (Here follows

¹ *Archives des Sciences Physiques et Naturelles* (1846).

a discussion on the constitution of nitric and sulphuric acids.) My experiments on ozone have shown that this body forms a peculiar compound with olefiant gas, without apparently oxidizing in the least either the hydrogen or the carbon of the gas. I had an idea that it would not be impossible that certain organic matters, exposed to a low temperature, would likewise form compounds, either with ozone alone, which, on my hypothesis, occurs in a state of combination or mixture in the acid mixture, or with NO_4 . It was this conjecture (doubtless very singular in the eyes of chemists) which principally led me to commence experiments with common sugar. I made a mixture of 1 volume of nitric acid (1.5) and 2 volumes of sulphuric acid (1.85), and cooled the mixture to 0°C . I then added some finely powdered sugar so as to form a paste. I stirred the whole and at the end of a few minutes the saccharine substance formed itself into a viscous mass, entirely separated from the acid liquid, without any disengagement of gas. The pasty mass was washed with boiling water until the latter no longer showed any acid reaction; after which I deprived it as much as possible, at a low temperature, of the water which it still retained. The substance now possessed the following properties: Exposed to a low temperature it is hard and brittle; at a moderate temperature it may be moulded like japlap resin, which gives it a beautifully silky lustre. It is semi-fluid at 100°C ; at high temperatures it gives off red vapour. Heated still more, it suddenly deflagrates with violence, without leaving any perceptible residue. It is almost insipid and colourless, transparent like the resins, almost insoluble in water, but easily soluble in essential oils, ether and concentrated nitric acid, and in most cases it acts in general like the resins from the chemical and physical point of view. Friction, for instance, renders it electrical. It should be added that the acid mixture, by means of which this resinous body was obtained, has an extremely marked bitter taste. I wished to make experiments also with other organic substances, and I soon discovered, one after another, all those about which there has been so much said of late in the French Academy. All this occurred in December 1845, and the first few months of 1846. In March I sent specimens of my new compound to some of my friends, especially Faraday, Herschel and Grove. It is necessary to note expressly that guncotton formed part of these products; but I must

add that hardly was it discovered, when I employed it in shooting experiments, the success of which encouraged me to continue them. Accepting the obliging invitation which I received I went to Wurtemberg, in the middle of April, and made experiments with guncotton, both in the Arsenal at Ludwigsburg, in the presence of artillery officers, and at Stuttgart before the King himself. In the course of May, June and July, with the kind co-operation of Commandant de Mechel, M. Burkhardt, captain of artillery, and other officers, I subsequently made in Bâle, numerous experiments with arms of small calibre, such as pistols, carbines, etc., and afterwards with mortars and cannon, experiments at which Baron de Krüdener, the Russian Ambassador, was several times present. I may be allowed to mention that I was the person who fired the first cannon loaded with guncotton and shot, on 28th July 1846, after we had previously ascertained by experiment with mortars that the substance in question was capable of being used with pieces of large calibre. About the same time, and independently, I employed guncotton to blast some rocks at Istein, in the Grand Duchy of Baden, and to blow up some old walls at Bâle, and in both cases I had opportunities of convincing myself, in the most satisfactory manner, of the superiority of this new explosive over gunpowder. In July I also made the first capsules and employed them with success for muskets in the presence of the above-named officers. Experiments of this kind, which took place frequently and in the presence of a great number of persons, could not long remain unknown, and the public journals soon gave, without participation on my part, descriptions more or less accurate of the results which I obtained. This circumstance, joined to the short notice which I inserted in the May number of *Poggendorff's Annalen*, could not fail to attract the attention of German chemists. In the middle of August I received from Böttger, Professor at Frankfort, the news that he had succeeded in preparing guncotton and other substances. Our two names thus became associated in the discovery of the substance in question. To Böttger, guncotton must have been particularly interesting, as he had previously discovered an organic acid which deflagrated readily. In August I went to England, where, assisted by the able engineer, Richard Taylor of Falmouth, I made numerous experiments, in the mines of Cornwall, which were entirely successful in the

opinion of all competent witnesses. Experiments on the action of guncotton were also made in several parts of England under my directions, both with small firearms and pieces of artillery, and the results obtained were very satisfactory. Until that time there had been little or nothing said of guncotton in France; and it would appear that the short notice which Grove gave at Southampton, at the meeting of the British Association, and the experiments with which he accompanied them, first served to attract the attention of French chemists to this substance. At Paris the thing was at first considered hardly credible, and jokes even were passed upon it. But when there could no longer remain any doubt as to the reality of the discovery, and when several chemists in Germany and other countries had published the processes which they employed to prepare guncotton, then a lively interest was manifested in a subject which had just before excited derision, and it was soon pretended that the new explosive was an old French discovery. It was declared to be nothing more than the xyloidine first discovered by Braconnot and afterwards investigated anew by Pelouze, and the only merit left to me was to have conceived the happy idea of putting this substance into a gunbarrel. The knowledge of the composition of xyloidine ought to have sufficed to have convinced those who put forward that opinion, that it is not suited for firearms on account of its containing too much carbon and too little oxygen, for the chief part to be converted during the combustion into gaseous matters. It was, moreover, very easy to discover the essential differences which exist between xyloidine and guncotton. Nevertheless the error was kept up for some months. Matters stood thus when on 4th November last, a Scotch chemist, Walter Crum of Glasgow, published a memoir in which he showed that guncotton is not the same product as xyloidine, but that it presents an essentially different composition, and towards the end of the same month the French Academy received a communication of the same nature. The guncotton was no longer xyloidine, it was called *pyroxyline*, and the first was admitted to be unsuitable for firearms. If, therefore, it is proved that from the commencement of 1846, I prepared guncotton and applied it to the discharge of firearms, and that Böttger did the same in August—if it be admitted that xyloidine cannot serve the

same purpose as guncotton, and if it be notoriously known that what is now called pyroxyline was not brought before the French Academy and the world until towards the middle of November last, the idea of attributing to France the discovery of guncotton cannot be seriously entertained, or of assigning to me merely a practical application of that which another had discovered. I appeal to the justice of Frenchmen to decide the point to whom belongs the honour, of not only being the first to apply the new substance in question but also of having first prepared it—to Braconnot and Pelouze or myself. I must, moreover, add expressly that it was not xyloidine, even, which led to my discovery, however intimate may be its relations with guncotton. It was theoretical ideas, possibly very erroneous ones, but which are peculiarly my own, as well as some facts which I was also the first to discover. *Suum cuique* is a principle of morality on which society at large rests; why should it not be strictly respected in the republic of science? Pelouze is a distinguished chemist and already possesses a sufficiently high reputation, not to require to elevate his pretensions on the merits of others; and I am fully persuaded that this esteemed chemist, of well known truth of character, will, approaching with impartiality the circumstances which have occurred, freely render me the justice to which I consider myself entitled."

CHAPTER IV

GUNCOTTON IN FRANCE (1846)

THE announcement of Schönbein's discovery aroused in the French Academy a remarkable interest. The *Comptes Rendus* of 1846 and 1847 contain a very large number of interesting communications on this particular subject, and it would be impossible, in a short space, to summarize them. Two communications, however, one by Dumas,¹ the other by Pelouze,² are of sufficient historical interest to be dealt with in detail. Schönbein wrote to Dumas as follows:—" You know, perhaps, that I have discovered a very simple method of transforming ordinary cotton into a material possessing all the necessary properties as a propellent. In addition to the superior explosive force of this curious substance, it is in every respect superior to the best powder. Experiments which I have made in mines and quarries and with cannons and mortars have shown that one pound of this substance produces effects equal to from 2 to 4 pounds of ordinary black powder. It should be added that cotton so treated does not leave any residue when exploded, and produces no smoke. The manufacture is not attended with the least danger, and does not require any costly installations. In view of these properties we cannot doubt that this explosive cotton should rapidly find a place in the pyrotechnic arts and especially on war vessels."

Dumas' own communication was as follows:—

"Arago having questioned me at the meeting of the Academy on 7th October 1846, on the subject of guncotton, I then stated that, although the details to hand were very meagre, I considered the subject to be one of very great importance, and that the new explosive substance would probably be found to be related to xyloidine discovered by Braconnot and further studied by Pelouze. It appeared to me to be only right to allow Schönbein to present the details of his discovery in the manner which he considered most convenient. Certain details of the

¹ *Compt. Rend.* (1846), 806-809. ² *Ibid.* (1846), 809-812 ; 892-902.

manufacture of guncotton have already been published in Germany, and I think it right that, as I have confirmed their accuracy, they should appear in the Transactions of the Academy. At the same time it will give an opportunity to Pelouze, to present to the Academy certain results which he has obtained as to the force of this new product. Otto, of Brunswick, gives the following details as to the preparation of guncotton. Concentrated fuming nitric acid, obtained by heating a mixture of 10 parts of saltpetre and 6 parts of sulphuric acid, has the property of converting cotton into an explosive. The acid first passing over acts most energetically in this respect. Cotton is dipped for half a minute in this acid. It is then pressed between two pieces of glass, washed until free from acid, and afterwards dried. The dry material will be found to be extremely explosive. Should a fresh quantity of cotton be dipped in the acid which has already been once used, it will be noted that the resulting product is only feebly explosive. If, however, this latter product is washed and dried and again dipped in acid, it will now be found to possess sufficiently strong explosive properties. The explosive property can be considerably increased by several dippings, and I have found that a product of extreme force is obtained after an immersion of 12 hours. A point of extreme importance is the care which ought to be exercised in washing the cotton. The last traces of acid are very difficult to remove, and should any remain it will be found that, on drying, the body smells strongly of oxides of nitrogen, and when ignited a strong acid smell is also produced. The best test for a sample of guncotton is to ignite it upon a porcelain plate. Should it burn slowly, leaving a residue upon the plate, it must be considered as unsatisfactory. A good guncotton burns very violently without leaving any residue. It is also of very great importance that when the guncotton is withdrawn from the acid, it should be washed immediately in a large quantity of water. Should small quantities of water be used it will be found that the guncotton becomes very hot, and that spots of a blue or green colour are produced, which are very difficult to remove, and the guncotton is very impure. Dr Knopp, of the University of Leipzig, gives the following details. Equal parts of English commercial sulphuric acid and commercial nitric acid are mixed in a porcelain basin. As much cotton is taken as can conveniently be dipped in the

liquid, and, after it is immersed, the basin is covered with a piece of glass. After standing for several minutes, at the ordinary temperature, the cotton is withdrawn and immediately washed in cold water. When dry it is extremely explosive.

Care should be taken that the cotton remains in the acid only sufficiently long to be partially dissolved. It would appear that a satisfactory guncotton can be obtained without observing any great exactitude as to the weight of the two acids and the time of immersion. On using a mixture containing a smaller proportion of sulphuric acid, and immersing the cotton for a shorter time, a satisfactory product was nevertheless obtained. Dr Bley of Bernberg has made experiments on the use of substances less costly than cotton. He has discovered that sawdust, treated in the same way as cotton, is converted into an explosive body which might very readily serve to replace ordinary powder in firearms and blasting."

Pelouze wrote as follows:—

" On a former occasion when noticing the discovery of this new explosive material, supposing it to be the product of nitric acid on cellulose (cotton, paper, lignin, etc.), I observed that it was undoubtedly the combustible substance which I described in 1838, and which must contain more oxygen, and therefore more nitric acid, than the xyloidine of Braconnot, *i.e.* the pulverulent and amorphous substance which that chemist obtained on precipitating by water a nitric acid solution of starch made in the cold, or one of cellulose effected at a higher temperature. This has proved to be the case. In what follows I shall attempt to show that the xyloidine of Braconnot and the substance which I obtained by impregnating various ligneous substances with concentrated nitric acid are not identical, as I with chemists in general long believed. I shall call *pyroxyline* or *pyroxyle* the product of monohydrated nitric acid on cotton, paper and ligneous substances, when this action has taken place without having caused the solution of the cellulose. Xyloidine will henceforth designate the substance obtained by Braconnot by precipitating the nitric acid solution of starch and other ligneous substances. The following are the differences observed between the two substances.

Xyloidine is very soluble in nitric acid, and this solution, which is quickly effected, becomes decomposed in the course of a day. Xyloidine is then converted into a deliquescent acid

which I described eight years ago. Pyroxyline does not dissolve even in considerable excess of nitric acid. It may be left in it for days without disappearing, or showing any loss of weight. Xyloidine, though very inflammable and detonating when struck, leaves, when heated in a retort, a considerable residue of carbon. Pyroxyline, as is well known, behaves quite differently. When heated from 175° to 180° C. it explodes violently, and its distillation in a retort is physically impossible. Xyloidine may be analysed, like any other substance, by means of copper oxide. Pyroxyline, under the same circumstances, breaks the tube even when quantities 100 times smaller are used. Five mgrms. of pyroxyline heated in a tube filled with mercury produced a violent detonation; whilst quantities far more considerable of xyloidine may be decomposed in this way without any danger. One hundred parts of dry starch, dissolved in concentrated nitric acid, and precipitated immediately on its solution, which is very rapid, yield, at most, 128 to 130 parts of xyloidine. One hundred parts of cellulose (paper, cotton) yield, either after a few minutes or several days' immersion in concentrated nitric acid, 168 to 170 parts of dry pyroxyline. These two experiments are the more characteristic, as the acid liquids, which rest above the pyroxyline and the xyloidine, contain nothing but mere traces of organic matter. Eight years ago I determined the composition of xyloidine. I concluded from my analysis that it might be represented by one equivalent of starch which had lost one equivalent of water and taken up one equivalent of nitric acid. I still believe this composition to be correct. However, xyloidine is amorphous, and insoluble in water. It is derived from a substance which is never perfectly pure, and is likewise amorphous and insoluble, and at present we possess no means of judging of the purity of a substance occurring under such unfavourable conditions. It is possible, therefore, that xyloidine and pyroxyline contain one and the same substance, the properties of which are more or less masked by the presence of some hitherto unknown substance. The point on which I insist is that the two compounds, in the state in which we are at present acquainted with them, differ too considerably to be considered identical. A Dutch chemist, Ballot, considers xyloidine to be a mixture of several substances, which have no longer any direct connection with starch. Be this as it may, the analysis of this chemist removed the com-

position of xyloidine from that of pyroxyline far more than mine. I selected some samples of cotton and paper which left but a mere trace of ash. I dried them at 115° C. and submitted them to the action of either concentrated nitric acid or a mixture of concentrated nitric acid and sulphuric acid. In ten experiments, which lasted from 10 minutes to 48 hours, the increase in weight of the cotton and the paper was practically the same. It was constantly comprised between 68 and 70 for every 100 parts of dry cotton or paper. This identity between cotton and paper, relative to the action of nitric acid, is not surprising, as paper, excepting traces of foreign matter, is nothing more than cotton the fibres of which have been more or less disintegrated. The remarkable fact in these experiments is the consistency of the results and the rapidity with which the compound is formed, notwithstanding its insolubility and that of the cellulose. It is in fact a true atomic relation between the elements of a combination effected by mere impregnation and under unusual circumstances. Admitting what appears to be true, that nitrated cellulose is the sole product which originates in the preceding reaction, calculation indicates that it must result from the combination of two equivalents of monohydrated nitric acid with one equivalent of cellulose minus one equivalent of water. Having endeavoured without success to analyse pyroxyline, I employed to determine the composition of this substance an indirect method, which, however, I believe to be unobjectionable. Having ascertained that 100 parts of cotton yield, on the average, 169 parts of dry inflammable substance, I neutralized the whole of the acid liquor in which I had immersed the cotton, and concentrated the resulting nitrate of ammonia in a glass retort, to which I had adapted a tube for collecting the gases. The ammonium nitrate was decomposed, just as if it were pure, into nitrous oxide and water. I was not able to detect the presence of carbonic acid in the gases, from which I concluded that no other organic substance was formed at the same time as the nitrated cellulose, and, as no gas is disengaged in the preparation, it may be concluded that it has, in fact, the composition above indicated. In summing up the preceding observations and experiments I think I am able to establish in a positive manner, that xyloidine and nitrated cellulose differ, not merely in their properties, but also in their composition. I had considered, with all chemists, that there

were merely some slight differences in these two substances arising from their different degree of cohesion and resistance to solvents, similar to what is manifested between starch and cellulose as proved by Payen, but this is not the case. They are in reality two bodies possessing different compositions and properties."

Pelouze then offers some remarks on the expense of producing the new substitute for gunpowder and sums up the history of its discovery as follows:—

"Xyloidine and pyroxyline are, as far as we are acquainted with them at present, not identical. Braconnot discovered xyloidine. I discovered the singular substance pyroxyline by a process entirely new and which no one before me had previously suspected. I pointed out its extreme combustibility and suggested its application in artillery. To Schönbein is due the honour of having shown that this substance constitutes an explosive material far more energetic than gunpowder. In conclusion, the only method as yet known for preparing this new explosive substance is that which I described in 1838, Schönbein having hitherto kept secret both the nature and method of preparation of his guncotton.

CHAPTER V

GUNCOTTON IN SCOTLAND (1847)

SCHÖNBEIN in his account of the steps leading to the discovery of guncotton, and the special work done upon this subject, mentions the name of Walter Crum¹ as showing that guncotton was quite different from the nitrostarch discovery by Braconnot and further investigated by Pelouze.

Crum's work is of very particular interest, not only on account of his thorough chemical investigation of guncotton, but also from the point of view that he devised the method which is now in universal use for the analysis of nitrates, nitric acid, and guncotton—the nitrometer. The original chemical notation is retained in this account of his paper, and, if it be borne in mind that the atomic weight of oxygen in Crum's time was taken as 8 and that the formula for nitre was KO. NO_5 , the figures in his paper can be very readily followed.

“At the first meeting of the present session of this Society I gave an account of some experimental inquiries into the nature of guncotton, a body whose composition was then little known. I had at that time chiefly occupied myself with its nitrous contents, and described a method by which some approximation could be made to a quantitative result for nitric acid. On resuming the subject I find that much was wanting to render the method a rigorously accurate one, and I shall now relate what I have since done to simplify and complete it. I shall first, however, give an account of its application to potassium nitrate, a body of known composition and easily obtained in a state of purity, to which I have had recourse as a means of proving the accuracy of the method and detecting any fallacy to which it might be liable.

Nitric Acid in Potassium Nitrate.—Purified by repeated crystallization and fused at a little more than its melting point. A glass jar 8 ins. long and $1\frac{1}{4}$ ins. in diameter is filled with, and inverted over, mercury. A single lump of

¹*Proc. Phil. Soc. Glasgow* (1847), 163.

fused nitrate, weighing about 6 grains, is first let up into it, and afterwards 50 grains of water. As soon as it is dissolved, sulphuric acid (125 grains), ascertained to be free from nitric acid, is added. By the action of the mercury on the liberated nitric acid, deutoxide of nitrogen soon begins to be evolved, and usually in about two hours, without the application of heat, the whole of the nitric acid is converted into that gas. Occasionally agitation is necessary, and it is easily performed by giving a jerking horizontal motion to the upper part of the jar. The surface of the sulphuric acid is then marked, and $\frac{3}{4}$ of a cubic inch of a solution of ferrous sulphate, recently boiled, is let up into the jar. The gas is rapidly absorbed, except a small portion, at last, which must be left several hours to the action of the solution, or be well shaken in a smaller tube with a fresh portion of it. No correction of deutoxide of nitrogen has to be made for moisture, for the mixture of the acid and water which I employed, and as I ascertained by direct experiment, has not perceptible force of vapour.

First Experiment.—5.4 grains of potassium nitrate yielded 4.975 cubic inches of gas at 60° F. and 30 inches. The residue not absorbed by ferrous sulphate equals 0.015 cubic inch, leaving 4.96 cubic inches of deutoxide of nitrogen, which is equal to 1.594 grains of NO_2 , and which corresponds to 2.869 grains of nitric acid, or 53.13% of the potassium nitrate. Four consecutive experiments gave 53.13, 53.14, 53.73, 53.29, mean 53.32.

The calculated percentage of nitric acid in nitre, the acid being taken at 6.75 and the potash at 5.8992, is 53.36. In order, further, to determine whether the presence of organic matter would interfere with the liberation of deutoxide of nitrogen, the experiment was repeated with the addition of 3 grains of cotton wool which was dissolved in the sulphuric acid. The result was 53.24. Other nitrates were analyzed in the same manner. For salts in powder which it is difficult to pass through the mercury without loss, I cut a $\frac{1}{4}$ in. glass tube into little cylinders of about $\frac{1}{2}$ in. long and closed up at the ends with thin paper fastened with gum. In the analysis of numerous samples of crude nitrates, the residue, which is azote, may be taken as a constant quantity, and the jar graduated in such a manner that the volume of gas may be read off at once as percentage of nitric acid.

Preparation of Guncotton. — The cotton I used was fine "Sea Island." It was first thoroughly carded and then bleached by boiling in caustic soda and put in a solution of bleaching powder; then caustic soda again, and afterwards weak nitric acid. It was well washed and beaten in a bag with water after each operation. When burnt, 10,000 parts left 9 of ash. It was considered to be lignin nearly pure. The cotton, dried and carded after bleaching, was exposed in parcels of 10 grains each for several hours to the heat of a steam bath, and each parcel was immersed, while hot, into a 1 oz. measure of the following mixture: Sulphuric acid (1·84) 1 measure, and 3 measures of pale lemon-coloured nitric acid (1·517).

After one hour it was washed in successive portions of water until no trace of acid remained, and was then dried in the open air. Thirty grains of bleached cotton waste dried at 65° F. became after some hours in the steam bath 28·32 grains, and lost therefore 5·6% of water. It increased to 51·08 grains when made into guncotton and dried in the open air. Dried further in a vacuum over sulphuric acid, it was reduced to 50·40 grains, and lost therefore 1·33% of water.

100 parts of dry cotton waste produced 177·9 parts of dry guncotton. Guncotton thus prepared is whiter but less transparent than the original bleached wool. It appears to be little liable to change, but a slight elevation of temperature causes a commencement of decomposition and the colour becomes more or less brown. It is much less tenacious than cotton wool. Dissolved in nitric acid and tested with barium chloride it gives no indication of sulphuric acid. The increase of weight above stated is the greatest I have been able to obtain, and I had completed its analysis in the manner I shall describe, when I found occasion to believe that it still contained a portion of unaltered cotton. With a view to saturate that portion it was immersed a second time for 24 hours in the same mixture of acid, but without yielding any greater quantity of nitric acid. An immersion of one hour in nitric acid gave a better result. It lost in weight by this second process 0·47%, but was little altered in appearance, and after being dried in the open air it lost in the air pump only 0·69% instead of 1·33% as in the former case. It is this substance of which I will now relate the analysis.

Ash in Guncotton.—16 grains of guncotton were dissolved in nitric acid. The solution evaporated by degrees and burnt to ashes left 0.035 grain of a reddish ash = 0.22%.

Nitric Acid in Guncotton.—In this process the same apparatus was employed as for potassium nitrate. About 6 grains of guncotton, containing a known quantity of water, are collected into a ball and squeezed between the finger and thumb to free it as much as possible from air, and let up into the jar over the mercury trough. 125 grains of sulphuric acid are added to it. Nitric acid is liberated, and, after being acted on by the mercury, produces oxide of nitrogen. After one hour, when about $\frac{3}{4}$ of the whole gas has been evolved and the guncotton is entirely dissolved, 50 grains of water are added. In another hour increase of gas ceases. In a few hours more its boundary is noted. It is then treated with ferrous sulphate solution and re-measured. The residue consists of azote from the common air introduced with the guncotton and a minute portion also which is always entangled between the mercury and the glass. Its oxygen is absorbed by the mercury when in the state of nitrous acid.

First Experiment.—6.02 grains of guncotton = 5.978 dried in a vacuum over sulphuric acid = 5.946 grains after deducting the ash, gave 5.513 cubic inches of gas at 30 inches and 60° F., of which 0.08 cubic inch was left by the ferrous sulphate. This represents, therefore, 5.433 cubic inches of deutoxide of nitrogen = 1.746 NO_2 , which represents 3.143 grains of nitric acid = 52.70%. The second experiment gave 52.68%. Guncotton, prepared by a single immersion, gave only 51.24% of nitric acid.

Carbon in Guncotton.—Having failed to obtain good results by burning this substance with copper oxide, I used chromate of lead, prepared from the nitrate, and heated to redness. I employed for the combustion an apparatus which I used many years ago for the analysis of indigo, and I still find it very convenient for such substances as do not require a strong red heat. It consists of a tube of hard glass 8 ins. long and $\frac{3}{8}$ in. in diameter, the gases from which are led, by a small bent tube, under the receiver in a mercury trough. One inch of the closed end of the tube is filled with 8 grains of chlorate ground with lead chromate; $4\frac{1}{2}$ ins. are filled with lead chromate among which is ground to powder 3 grains of guncotton; $1\frac{1}{2}$ ins. contain

lead chromate used to wash out the mortar. A glass plug separates these materials from the perforated cork which joins the two tubes. The materials are gradually heated with a broad-wicked spirit lamp. Carbon dioxide comes over mixed, when, in the receiver, with NO_2 , and the azote of the apparatus, and when all the guncotton is consumed the lamps are extended to the chlorate. The oxygen gas thus liberated, which, in other cases, is useful to consume carbonaceous matter that may have escaped the chromate, expels, in this case, all remains of carbon dioxide, and passing itself into the receiver, mixes there with NO_2 and causes its entire absorption by mercury. Oxygen and azote are then the only gases left with carbon dioxide, and, as they are not absorbable, an addition of $\frac{1}{2}$ cubic inch of caustic soda indicates exactly the quantity of carbon dioxide present. In one experiment 2.993 grains of guncotton (after deducting water and ashes) yielded 7.972 cubic inches of gas, of which 5.733 were carbon dioxide = 0.739 grain of carbon, or 24.69%. A second estimation gave 25.16 mean = 24.92%.

Elements of Water in Guncotton.—To burn guncotton for the purpose of collecting its oxygen and hydrogen in a state of water, I ground up 10 grains with powdered flint, and used the combustion tube already described, having attached to it a calcium chloride tube, and afterwards a tube with asbestos moistened with sulphuric acid. But, along with the water, ammonia and other matters were obtained which destroyed the result. I next used a thin glass tube of $1\frac{1}{2}$ inches long, bent so that one inch in the middle would dip into cold water. Such water as would condense at 65° F. was collected. The gas was led through it into a mercurial trough and measured.

A trace of cyanogen appeared in the last portion of the gas, while the oxygen from the chlorate was burning a quantity of carbon that had escaped the nitric acid. After the experiments the refrigerating tube was found studded with crystals of bicarbonate of ammonia. It contained very little water in the liquid state. The crystals and liquid were washed out with water, converted into muriate of ammonia, and were found to contain 0.675 grain of ammonium carbonate, the hydrogen of which represents 0.299 grain of water. There was besides 2.025 grains of water in the tube; and in the 22 inches of gas which were obtained, assuming it to be saturated with moisture, which is doubtful, there was 0.088 grain, making in all 2.412

grains, from which must be deducted 0.160 grain hygrometric water in the guncotton and flint, leaving 2.25 grains for the water in 9.92 grains of dry guncotton, or 22.7%. In a second experiment, where the only difference was in having moistened cotton for the gas to pass through, before entering the mercury trough, the water obtained only amounted to 20.61%. I did not proceed further. These were the two last of a number of experiments, and the determination of nitric acid and carbon are so much more satisfactory that I prefer resting the water content on this result. The experiments I have related give the following for the composition of guncotton:—

52.69 nitric acid
24.92 carbon
22.39 water
<hr/>
100.00

These numbers are nearly in the proportion of 12 C, 7 HO, 3 NO₅.

Found.	Calculated.
52.69	52.69 = 3 NO ₅ .
24.92	23.41 = 12 C.
22.39	20.49 = 7 HO.
<hr/>	<hr/>
100.00	96.59

Leaving a remainder of 3.41%, consisting of 1.51% carbon and 1.9% water. These, however, are nearly in the proportion which form lignin.

Found.	Calculated.
1.51	1.51 = 12 C
1.90	1.88 = 10 HO
	} = Lignin.

Guncotton, from the form in which it is produced, is not one of those substances we can expect to obtain in absolute purity. Every previous improvement in its preparation had diminished the excess of unaltered cotton, and I have no reason to suppose the last portion perfect, considering the difficulty with which some of the previous stages of improvement have been attained. The specimen I have thus examined consists, therefore, of—

96.59 guncotton
3.41 lignin

And pure guncotton consists of—

24.24 = 12 C.	24.24 = 12 C.
21.21 = 7 H ₂ O.	2.36 = 7 H.
54.55 = 3 NO ₅ .	14.14 = 3 N.
	59.26 = 22 O.
<hr/> 100.00	<hr/> 100.00

It is lignin in which three atoms of water are replaced by three atoms of nitric acid.

Crum's results for guncotton, in our present notation, are as follows :—

For Cellulose Trinitrate.	Calculated.	Obtained by Crum.
Carbon .	24.24	24.92
Hydrogen .	2.36	2.49
Nitrogen .	14.14	13.69 (by nitrometer)
Oxygen .	59.26	58.90

CHAPTER VI

GUNCOTTON IN ENGLAND (1846-7)

Two interesting papers were published in England, shortly after Schönbein's discovery, on the subject of guncotton. Teschemacher's¹ paper is worthy of note because he proves from his experiments that it is nitric acid alone which, in the mixed acids, enters into the reaction in the formation of guncotton. Gladstone's² communication stands on the same basis as the work of Crum in its thorough chemical investigation of the composition and properties of guncotton.

Teschemacher wrote as follows:—"In consequence of the discovery by Professor Schönbein of guncotton, and of the possibility of its substitution in many cases for gunpowder, I have been induced to enter into an examination of the mode of its formation and of its synthetical composition, principally with a view of ascertaining how far it would be likely to affect an important branch of trade—the production and value of saltpetre and nitrate of soda. The examination was not commenced with the view of publishing it, but some of the facts brought to light appeared to possess sufficient interest to lay before the Society. I must premise that the experiments relate only to the guncotton prepared by the process recommended by Mr T. Taylor. Equal measure of nitric acid of sp. gr. 1.509, and of sulphuric acid sp. gr. 1.840, were mixed together, and constituted (No. 1) the acids used in these experiments. I dried 50 grs. of South American cotton (from La Guayra) over a water-bath, and found the cotton gave off 3.40 grs. of hygrometric water. The 46.60 grs. of cotton which remained after drying, I steeped in 487½ grs. of the mixed acids No. 1; the strong acids were in contact with the cotton about two minutes, and after squeezing well, the cotton was washed in water to free it from the acid: the quantity of water used was 5000 grs. The strong acid squeezed out of the cotton weighed 113½ grs. (No. 2), leaving 374 grs. of acid (No. 3) to be accounted for, to make up the

¹ *Memoirs of the Chem. Soc.* (1846), 253.

² *Ibid.* (1847), 412.

original quantity used. The cotton thus prepared was perfectly dried in the air over a water-bath, and was found to weigh 79 grs., being an increase of 32.40 grs. on the cotton used, equal to an increase of $69\frac{1}{2}$ grs. upon every 100 grs. of cotton in its original state. To ascertain whether the cotton would absorb anything more, I steeped 25 grs. of the above cotton, after it had been washed and dried, in fresh acid (No. 1), but no increase of weight took place. I also steeped a fresh portion of cotton for three minutes in the same quantity of fresh acid (No. 1), it weighed after washing and drying 78 grs.; a third portion was steeped for four minutes in one-third more acid than in the previous experiments, it weighed after washing 79 grs.; so that it appeared that the cotton had taken up its maximum from the acid by the first immersion.

As these 32.40 grs. increase of weight were clearly derived from the $487\frac{1}{2}$ grs. of the mixed acids, I made the following experiments to ascertain what alteration the acids had undergone. I neutralized 100 grs. by weight of the original acid (No. 1) by carbonate of soda, and found that it required 52.80 grs. of soda for that purpose. I found likewise that to neutralize the $113\frac{1}{2}$ grs. of strong acid (No. 2) separated from the cotton required 58.52 grs. of soda, and that the remaining 374 grs. of acid to be accounted for, contained in the washings, required 170.30 grs. of soda for neutralization, making together 228.82 grs. of soda required to neutralize the $487\frac{1}{2}$ grs. of acids No. 2 and 3, used for acting upon the cotton; therefore, if 100 grs. of the original mixed acids (No. 1) required 52.80 grs. of soda as above for neutralization, $487\frac{1}{2}$ grs. would require (if not acted upon by the cotton) 257.36 grs. of soda; it, however, only required 228.82 grs. as above. The difference, 28.54 grs. of soda, is therefore equal to the acid which disappeared, or was taken up by the immersion of 46.60 grs. of cotton in the mixed acids. To ascertain whether a portion of each of the mixed acids, or only one of them, was taken up by the cotton, I added to the solution of the 100 grs. of mixed acids (No. 1) (neutralized by the soda) chloride of barium, and obtained a precipitate weighing 126 grs. of sulphate of barytes.

I also, in the same manner, precipitated from the solution No. 2, 165.40 grs. of sulphate of barytes, and from No. 3, of 374 grs., 449.30 grs. of sulphate of barytes, making together 614.70 grs.; therefore, if 100 grs. of the original acids (No. 1)

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give 126 grs. of sulphate of barytes, $487\frac{1}{2}$ grs. would give 614·25 grs.; they gave, as above, 614·70 grs., showing that no portions of the sulphuric acid were withdrawn, but that it was a portion of the ingredients of the nitric acid alone that combined with the cotton. The quantity of soda neutralized by the acids (Nos. 2 and 3) was, as just stated, 28·54 grs.; therefore, if 32 grs. of soda neutralize 54 grs. of nitric acid, 28·54 grs. of soda will give 48 grs. of nitric acid, the quantity of acid which disappeared, or was taken up by the cotton. From what took place, the following may be deduced as its synthetical composition:—48 grs. of dry nitric acid, containing 35·66 grs. of oxygen, were decomposed by the 46·60 grs. of cotton, and 32·40 grs. were added to the weight of the cotton. It is probable that the mixed acids combined with a portion of the constituent water of the cotton, which was replaced by oxygen and nitrogen, in the proportions of nitric acid, as there was no appearance of the evolution of either nitrogen or oxygen in the formation of the guncotton. Its synthetical composition would stand thus:—

46·60 grs. of cotton deprived of
15·60 water, give

31·00 cotton without constitutional water, combined with
48·00 oxygen and nitrogen derived from the mixed acids

79·00 the weight of guncotton produced, equal to

39·25 parts cotton,
60·75 „ oxygen and nitrogen (nitric acid)

in 100·00 parts.

From these experiments we arrive at the following conclusions regarding the formation of this substance:—That as it requires 48 grs. of nitric acid, or its equivalent 90·66 grs. of saltpetre, to form 79 grs. of guncotton, it will require 60·75 grs. of nitric acid, or its equivalent 114·76 grs. of saltpetre, to form 100 grs. of guncotton; and according to the same calculation, it will require 97·76 grs. of nitrate of soda for the same purpose. Taking into consideration the original cost of the cotton, the expensive manipulation of the conversion of the nitre into

nitric acid, and the additional weight of nitre required to produce the same weight of guncotton, it is evident that the latter substance must be more expensive than gunpowder, taking weight for weight of each. How far, however, guncotton may exceed gunpowder in its explosive force still remains to be ascertained, and this of course forms an important element in the calculation. Other processes may be already known, or may be hereafter discovered, calculated to reduce the expenses of the formation of the so-called guncotton, but it must be still borne in mind that an enormous quantity of oxygen, amounting to 45 parts in every 100 parts of guncotton produced, must be obtained from some extraneous source for combination.

Many other vegetable fibres may be substituted for cotton; but from the few experiments which I have made, it appears they do not possess the explosive force of cotton. In a trial upon flax, I found that 50 grs. increased in weight to 72 grs.; the explosive force was feeble; this was the case with sawdust similarly prepared; but it is possible that this latter form of impure lignin may eventually be of more importance than it appears at present. Fifty grains of deal sawdust dried at 212° were first washed with dilute muriatic acid and then with dilute caustic alkali; they were found to have lost 6 grs. after washing and again drying. The 44 grs. remaining were steeped in the mixed acids for about five minutes, then washed and dried: they increased to 58.7 grs. The acids were examined by carbonate of soda in the manner before detailed, the sawdust was found to have neutralized 22.90 grs. of soda, equal to 38.65 parts of nitric acid, or 66.66 of nitric acid for every 100 parts of gun sawdust. This gun sawdust flashed off readily, but with less rapidity than guncotton, leaving a small carbonaceous residue. The difference in quantity of nitric acid taken up by the sawdust and the cotton is no doubt owing to the former being a much more impure form of lignin than the latter."

Gladstone published the following work:—

"At the commencement of the present year, having perceived that considerable doubt rested on the ultimate composition of guncotton, I undertook a series of experiments with a view to ascertain it, if possible; and during my investigation my attention was drawn to various papers that appeared on the subject, where I found contradictory accounts, not only of the results of analysis, but also of the action of various re-

puted solvents. The experiments detailed below, although they are far from exhausting the subject, may serve to explain some of these anomalies, and to point out a few facts, which, as far as I have been able to learn, have not been hitherto noticed.

The cotton employed was that used by jewellers, well-carded, perfectly white, and free from imperfections. An analysis of the substance by combustion with oxide of copper in a stream of oxygen yielded the following results:—

Cotton employed	3.16	grs.
Carbonic acid produced	5.14	„
Water produced	2.06	„

These proportions are—

Carbon	44.37
Hydrogen	7.24
Oxygen	48.39
	<hr/>
	100.00

Lignin calculated from the formula $C_{24}H_{20}O_{20}$:—

Carbon	44.44
Hydrogen	6.17
Oxygen	49.39
	<hr/>
	100.00

The excess of hydrogen doubtless arises from moisture absorbed by the oxide of copper during the unavoidable delay in mixing it with the cotton. This cotton, which may be considered as pure lignin, was steeped until thoroughly wetted in a mixture of nitric acid of sp. gr. 1.502, and nearly an equal bulk of strong sulphuric acid, then well washed with water, and dried at a temperature not exceeding 212° F. In one instance 38.38 grs. of cotton became 66.84 grs., being an increase of 28.46 grs., or 74.15 per cent. In a second experiment 59.3 grs. of cotton gave an increase of 43.7 grs., or 73.7 per cent. The guncotton, or pyroxyline, thus produced resembled the original cotton in physical properties very closely, and exploded at about 370° F., producing no smoke and leaving no residue.

The action of various solvents and reagents upon this substance was found to be as follows:—It is absolutely insoluble in pure water, and nearly so in strong alcohol, ether, whether hydrated or anhydrous, and in a mixture of ether with $\frac{1}{10}$ part

of alcohol; but acetic ether instantly destroys its fibre, and dissolves it in large quantities. The solution yields on spontaneous evaporation a white powder of the same weight as the original pyroxyline, but I have found it very difficult to drive off the last traces of the solvent. The action of sulphuric acid upon it differs from that exerted upon unaltered cotton; for, while the latter is instantly dissolved by the strong acid, and charred upon a slight elevation of temperature, pyroxyline dissolves with difficulty unless the acid be warmed, evolving at the same time nitric oxide and other gases, and not being charred even upon boiling. With the aid of heat it dissolves immediately in a solution of potash. By means of these three last-mentioned tests I was able to prove the absence of any unaltered cotton in the product under examination. The action of other reagents upon guncotton was not so decided; it was dissolved, but not without long boiling, by ammonia, the alkaline carbonates, hydrochloric acid, acetic acid, both glacial and dilute, and weak sulphuric acid. These solutions, as well as the two preceding, contained nitric acid; nothing could be precipitated from them by dilution or neutralization; and when evaporated they yielded only a dark brown amorphous matter. It is evident that none of these reagents restore the lignin in its original condition; and they do not afford any means of ascertaining whether the compound contains the elements of nitric or hyponitric acid.

As there exists a great discrepancy in the accounts given of the increase of weight in making guncotton, I examined whether the length of time it was immersed in the acid liquor, or the proportions of the acids employed, were the cause. The length of immersion I found to produce no alteration; but upon employing two measures of sulphuric acid to one of nitric acid, I obtained a product resembling in all respects ordinary pyroxyline, yet 42.77 grs. gave an increase of only 24.31 grs., or 56.84 per cent. Upon repetition of this experiment I found the increase to be 59.93 per cent., and again 70.6 per cent. Suspecting from the disparity of these results that something might be dissolved in the acid liquor, I immersed 6.7 grs. of cotton in a large quantity of the mixed acids, but it increased 4.9 grs., or 73.1 per cent. Perceiving that I had obtained an opposite effect to that anticipated, I treated 12.64 grs. of cotton with just sufficient of the mixture to wet it thoroughly: the fibre

was evidently somewhat destroyed; the increase in weight was only 6.54 grs., or 51.74 per cent., and the acid liquor squeezed from the cotton, neutralized with ammonia, evaporated to dryness, and heated, gave abundant evidence of organic matter being present. Lest, however, it might be supposed that the whole had not been converted into pyroxyline, it was treated again with the mixed acids, but that produced an increase of only 0.12 gr. The action of various solvents confirmed its identity with ordinary pyroxyline, while its solubility in potash proved that the transformation had been very nearly complete. A repetition of the experiment gave similar results. It thus appears that the small increase in weight in the preparation of pyroxyline takes place when there is not sufficient nitric acid present to prevent the peculiar action of the sulphuric acid, namely, that of dissolving and altering it. When, however, the increase amounted to about 74 per cent., I was never able to detect the presence of oxalic acid or other organic matter in the acid liquor; and as no gas is evolved during the preparation of pyroxyline, it may be concluded that there is no secondary product containing carbon.

Subsequently, when Dr Schönbein had specified his method of making guncotton, I treated 18.78 grs. of cotton with a mixture of three parts of sulphuric acid and one of nitric acid, sp. gr. 1.5, following his directions. The result was 32.92 grs. of a substance similar to that produced in former experiments, being an increase of 75.20 per cent. On another occasion 80.95 grs. of cotton gave an increase of 61.10 grs., or 75.47 per cent. The action of solvents and reagents confirmed the identity of this pyroxyline with that obtained in my previous experiments, and I was equally able to establish the absence of any secondary product containing carbon. In determining the ultimate composition of pyroxyline several precautions were found to be necessary. In the analyses recorded below it was cut into small pieces, and, after the weight was taken, mixed carefully with oxide of copper. To prevent its caking together the admixture of a little asbestos was found useful. This was introduced into a long combustion-tube, then some fresh oxide of copper, and upon it again some fused into lumps so as to fill the whole bore for about 7 inches. Lastly was added a mixture of copper turnings and reduced copper for about 9 inches. The combustion, conducted cautiously in the

usual manner, gave the following results; the pyroxyline burnt in the sixth experiment having been prepared by Schönbein's method.

	I.	II.	III.	IV.	V.	VI.
Pyroxyline employed . . .	4.09	4.61	3.57	4.85	4.55	2.905
Carbonic Acid produced . .	4.20	4.52	3.42	4.88	—	2.84
Water produced	1.19	1.36	—	—	1.34	0.87

Hence in 100 parts—

	I.	II.	III.	IV.	V.	VI.
Carbon	27.90	26.74	26.10	27.44	—	26.65
Hydrogen	3.22	3.27	—	—	3.27	3.32

In order to determine the amount of nitrogen the differential mode was adopted, as the method of Will and Varrentrapp is inapplicable to substances containing this element in so highly oxidized a state. The same precautions were taken as in the estimation of carbon; and the collected gases gave the following results after due correction for barometrical pressure:—

	I.	II.	Another Specimen
Carbonic Acid	25.0	38.5	23.9
Nitrogen	5.5	8.5	5.1

These proportions are—

Nitrogen.		Carbonic Acid.
1	:	4.55
1	:	4.53
1	:	4.68

The volumes of the gases represent respectively equivalents of carbon and nitrogen, and since no secondary product is formed in the conversion of lignin into pyroxyline, the 24 equivalents of carbon in the former must be found in the latter. This will give the following ratio in equivalents of carbon and nitrogen according to the three experiments above cited:—

	I.	II.	III.
Carbon	24.0	24.0	24.0
Nitrogen	5.28	5.3	5.12

or 24:5, which accords with the proportions assigned by Pelouze. The formula which best agrees with these results is the following:— $C_{24} \left\{ \begin{smallmatrix} H_{15} \\ 5NO_4 \end{smallmatrix} \right\} O_{20}$, which, reckoned to 100 parts, gives—

Carbon	26.23
Hydrogen	2.73
Nitrogen	12.75
Oxygen	58.29

In order to compare pyroxyline with xyloidine, I treated starch with fuming nitric acid until the whole was converted into a gelatinous mass. The addition of water then threw down a white powder, which was subsequently well-washed and dried. The iodine test proved the absence of all unaltered starch. The xyloidine thus obtained explodes at about 360° F., leaving a carbonaceous residue. It is slightly soluble in ether, with which it is capable of forming a peculiar compound not yet investigated; more so in alcohol, but most of all in ether mixed with a small proportion of alcohol, or in acetic ether. It is dissolved by strong sulphuric acid without the aid of heat, and by boiling solutions of potash, ammonia, hydrochloric acid and dilute sulphuric acid. These solutions contain nitric acid, and nothing is precipitated from them by dilution or neutralization. Xyloidine is also soluble in strong acetic acid, or in nitric acid, whether fuming or of sp. gr. 1.25, but is reprecipitated from either by dilution. It was also found that nitric acid of ordinary strength (sp. gr. 1.45) answered equally well in the preparation of this substance; but when acid of sp. gr. 1.41 was employed no such result was obtained. Starch treated with a mixture of equal measures of nitric and sulphuric acids produced a substance of greater combustibility, and more closely resembling pyroxyline, but differing from it in being soluble in glacial acetic acid, and in a mixture of ether with one-tenth part of alcohol, as also in the action that acetic ether exerts upon it. Xyloidine also, when subjected to the mixed acids, gave a product identical with the above, as far at least as the action of solvents can prove.

Xyloidine burnt by means of oxide of copper, with the usual precautions, gave the following results. The substance employed in the third experiment was made from arrow-root.

	I.	II.	III.
Xyloidine employed . . .	4.77	5.23	6.75
Carbonic Acid produced . . .	5.30	5.91	7.87
Water produced . . .	1.84	1.96	2.80
Hence in 100 parts—			

	I.	II.	III.
Carbon	30.30	30.82	31.79
Hydrogen	4.28	4.16	4.60

In the determination of nitrogen by the differential method the proportions of the gases obtained were—

	I.	II.	III.
Carbonic Acid	70.7	53.4	53.8
Nitrogen	10.6	6.9	8.0

These are in the proportion of—

	I.	II.	III.
Carbon	24.0	24.0	24.0
Nitrogen	3.59	3.10	3.57

These numbers suggest the simple substitution product $C_{24} \left\{ \begin{smallmatrix} H_{17} \\ 3NO_4 \end{smallmatrix} \right\} O_{20}$, in which the percentage of carbon would be

31.37, and of hydrogen 3.70; yet the amount of nitrogen is somewhat too great, and there is far from being sufficient evidence to prove the definiteness of the substance itself. The wide difference also in the results obtained by various chemists can scarcely be accounted for, except upon the supposition that they have operated upon very different substances.

The solubility of xyloidine in nitric acid led me to examine whether any alteration could be effected upon pyroxyline by similar means. The most dilute acid which I found to have any effect upon it in the cold was that of sp. gr. 1.414; but the alteration took place by means of this only after long standing, and but to a slight extent. Nitric acid of sp. gr. 1.45, however, is capable of dissolving pyroxyline, and alters both its composition and properties, as will be presently described; whilst fuming nitric acid has not the slightest effect upon it. The new product just mentioned is acted upon somewhat differently by various solvents, according to whether it exists in a fibrous condition, or in powder as precipitated from solution; yet I have found by experiment that no alteration in weight is effected by this change of condition. When in fibre it is slightly soluble in strong alcohol, ether, a mixture of ether with $\frac{1}{16}$ part of

alcohol, and acetic ether, but when in the pulverulent state it is very soluble in these menstrua, and in glacial acetic acid. In either condition it leaves a carbonaceous residue on combustion, is dissolved by nitric acid, whether of sp. gr. 1.25 or 1.5, and reprecipitated upon dilution. Strong sulphuric acid also dissolves it in the cold, and chars it at a temperature below 180°. These two last properties show that the original pyroxyline was perfectly free from admixture with this new substance.

There occurs a considerable decrease of weight through this transformation. In the first experiment 32 grs. of substance operated upon gave 25.82 grs. of the new product; in the second 43.64 grs. of the one yielded 34.68 of the other. Now assuming the increase in the preparation of pyroxyline to be 75 per cent., the weight of the new product above that of the original cotton would be, as calculated from these figures, 41.1 and 39.05 per cent. When this new product, whether in the fibrous or the pulverulent condition, was treated with a mixture of equal parts of nitric and sulphuric acids, it increased considerably in weight, and the resulting substance had all the properties of pyroxyline as prepared in the usual manner. 11.16 grs. of the one yielded 13.56 grs. of the other; the quantity that should theoretically have been obtained, calculating it from the decrease in making the new product, is 13.84 or 14.04 grs. Again, 12.35 grs. of the substance as precipitated from solution gave 15.75 grs.; the theoretical amount would have been 15.31 or 15.54 grs. This result proves the distinctness of the new product from xyloidine, a fact that could not have been ascertained from the action of the before mentioned solvents.

Whilst engaged in obtaining these results, I also examined the action of nitric acid of various degrees of strength upon pure cotton. By treating it with nitric acid of sp. gr. 1.5 I obtained a product evidently different from guncotton, but as it did not appear to be homogeneous throughout, I passed on to investigate the action of a weaker acid. That of sp. gr. 1.45 gave a substance which proved to be identical with the product of the action of the same acid upon pyroxyline. Upon a repetition of the experiment 68.54 grs. increased in weight 14.61 grs., or 21.31 per cent.—a smaller increase than might have been anticipated, but which may easily be accounted for by the fact that the whole cotton had not been transformed,

as was proved by a considerable portion being left undissolved by a boiling solution of potash. Nitric acid of sp. gr. 1·414 produced the same alteration, but only to a small extent, and after long standing. 23·75 grs. of cotton soaked in nitric acid of sp. gr. 1·516 became a hard mass, and increased in weight 13·49 grs., or 56·8 per cent.; the action of various solvents upon the resulting substance indicated that it was a mixture of pyroxyline and the new product. On another occasion, when the transformation by means of nitric acid of sp. gr. 1·47 proved to be complete, 29·52 grs. of cotton increased 9·51 grs., or 32·89 per cent. But in order to obtain a substance sufficiently pure for analysis 16·29 grs. of cotton were treated with enough nitric acid to dissolve the whole; the new product was precipitated by dilution, and the increase in weight was found to be 5·34 grs., or 32·78 per cent. In these instances there occurred a secondary product containing carbon not precipitable by water.

When this was subjected to combustion with oxide of copper the following results were obtained:—

	I.	II.	Another Specimen.
Substance employed .	3·15	2·985	3·165
Carbonic Acid produced .	3·58	3·39	3·55
Water produced . . .	1·00	1·01	1·14

Hence in 100 parts—

Carbon	30·99	30·97	30·59
Hydrogen	3·52	3·75	4·00

I was unable to obtain any very accurate estimation of nitrogen by the differential method: the results most to be depended upon were—

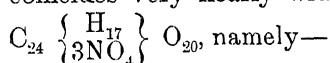
Carbonic Acid	120·7	76·7
Nitrogen	13·6	8·3

In the proportion of—

Carbon	24·0	24·0
Nitrogen	2·7	2·6

These numbers lead me to think that there are three equivalents of nitrogen in the compound, especially as I observed during the combustion that the substance became charred even 1 or 2 inches beyond the glowing charcoal, which will

account for the deficiency of nitrogen when compared with the carbonic acid. Hence the composition of the new product coincides very nearly with that calculated from the formula



Carbon	31.37
Hydrogen	3.70
Nitrogen	9.15
Oxygen	55.78
	<hr/>
	100.00

Under this supposition the increase in weight in the preparation would be 41.66 per cent.; very similar to that calculated from the results obtained by the action of nitric acid of sp. gr. 1.45 on pyroxyline, namely, 39.05 and 41.1 per cent. In order to add an additional proof of the identity of the two substances obtained by the action of nitric acid of sp. gr. 1.45 on cotton and on pyroxyline, and also of the fact that pyroxyline is reproduced by the action of mixed sulphuric and nitric acids upon the new product, the experiment was repeated with a portion of the substance made from pure cotton: the result was pyroxyline. In the transformation 26.56 grs. became 38.04; now these 26.56 grs. were produced from 21.80 grs. of the original cotton; hence the increase upon the cotton itself would be 16.23 grs., or 74.4 per cent., coinciding with the amount usually obtained in the preparation of pyroxyline.

I. From these results it appears that in the treatment of woody fibre by nitric acid raised to its highest degree of strength by the addition of sulphuric acid, 5 equivalents of the acid combine with 1 of lignin to produce pyroxyline displacing 5 equivalents of the elements of water, as indicated by the formula $\text{C}_{24} \left\{ \begin{array}{c} \text{H}_{15} \\ 5\text{NO}_4 \end{array} \right\} \text{O}_{20}$. The amount per cent. of carbon and hydrogen hence deduced closely agrees also with that assigned by Ransome¹ and Pettenkofer.²

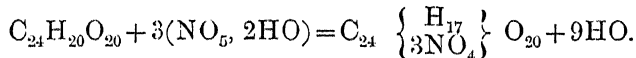
	Calculated.	Ransome.	Pettenkofer
Carbon	26.23	26.28	26.26
Hydrogen	2.73	3.16	2.75

¹ *Phil. Mag.*, January 1847.

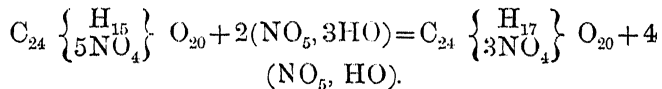
² *Pharmaceutisches Central Blatt*, 30th December 1846.

In this case the synthetical experiment would give an increase of 69.44 per cent.—nearly the amount obtained in the best experiments. My own analyses, however, have yielded a somewhat larger amount of carbon.

II. If lignin be treated with nitric acid combined with more than 1 equivalent of water, another compound is produced, containing a smaller proportion of the elements of nitric acid, most probably $C_{24} \left\{ \begin{smallmatrix} H_{17} \\ 3NO_4 \end{smallmatrix} \right\} O_{20}$, and very closely resembling, but not identical with, pyroxyline.



Also if pyroxyline itself be treated with nitric acid containing 3 equivalents of water, the same compound results:—



And this transformation may be reversed.

Whilst completing my examination of this substance, my attention was drawn to the communication of Payen in the *Comptes Rendus* of 25th January, where some properties of 'Coton hypoazotique' are described. It is possibly the same; yet, in order to express its distinctness from pyroxyline, I would propose as the appellation of my substance cotton-xloldine."

CHAPTER VII

THE PATENTS OF SCHÖNBEIN (1846), TONKIN (1862), AND ABEL (1865)

SCHÖNBEIN did not take out a patent in England for the manufacture of guncotton in his own name, but in that of John Taylor.¹ This patent is of such importance that it may very justly be dealt with in detail. "The invention consists of a manufacture of an explosive compound applicable to mining purposes, the throwing of projectiles, or otherwise, as a substitute for gunpowder, by treating or combining matters of vegetable origin with acids. The vegetable matter which is found best suited for the purpose of the invention is cotton, in the state in which it comes into this country, but cleaned from any extraneous matter, it being desirable to operate only on the clean fibre of the cotton, which should be dry. The acids I employed are a nitric acid of from 1.45 to 1.5 sp. gr., and sulphuric acid of 1.85 sp. gr. As far as my experience goes the best mode of using them is to mix them in the proportions of one measure of the nitric acid with three measures of the sulphuric acid, in a convenient vessel of glazed earthenware, or other material not acted on by acids. By this admixture great heat will be produced. The mixture should be allowed to cool until it reaches a temperature of from 50° to 60° F. The cotton should then be immersed in the acids so mixed, so as to become thoroughly impregnated therewith. It should be introduced as open as practicable, and in order to ensure the cotton being fully impregnated with the acids and every part equally and fully subjected to the action thereto, the cotton when in the acids is to be moved or stirred by means of a rod of glass, or other material not acted on by the acids. The acids are then to be pressed or drawn off. The cotton is to be gently pressed in the vessel containing it, by a presser of glazed earthenware, or other material not acted on by the acids, in

¹ *Improvements in the Manufacture of Explosive Compounds*, communicated to me from a certain foreigner residing abroad. John Taylor of Adelphi, Middlesex. English patent 11407, 8th October 1846.

order to free it in part from the acids, and is next to be covered and left to stand for about an hour, when it is again to be pressed in order to remove as much of the acids therefrom as practicable, after which the cotton is to be washed in a continuous flow of water, and well agitated or stirred therein until the water does not indicate the presence of any acid by the ordinary test of litmus paper. The cotton is now again to be pressed to free it from the water as much as possible, and in order to ensure the cotton being perfectly free from uncombined acid it is to be dipped in a very weak solution of potassium carbonate (1 oz. to 1 gall.). The cotton is now to be partially dried, which is conveniently done by subjecting it to a press, to press out the solution of potassium carbonate. Though the prepared cotton when fully dried has already become highly explosive, it should next be immersed and well stirred in a very weak solution of pure potassium nitrate (1 oz. to 1 gall.). The use of this solution appears to add strength to the compound, but the use of this solution and also potassium carbonate are not essential and may be dispensed with. The cotton is again to be pressed to remove the solution, and is afterwards to be opened out and dried, which may be conveniently done by spreading it thinly on surfaces in a room heated by steam or otherwise to about 150° F., and when dried it is fit for use. I would remark that nitric acid alone produces on cotton an effect similar to that produced on cotton by the mixtures of acids above mentioned, but in carrying out the invention with nitric acid alone, the cotton should be removed and washed immediately after it has been soaked with acid; but I believe that so good a result cannot be obtained by the use of nitric acid alone, and the product is most costly. I do not restrict the invention to the use of cotton, although I have confined my description to the employment of cotton, because of its cheapness and peculiar applicability for the purpose; other matters of vegetable origin may be converted into explosive compounds by the same acids, and may therefore be used, though as far as my experience goes, not with so beneficial a result. Neither do I confine myself to the above-mentioned specific gravity of acids; acids of inferior gravity may be used, though as far as my experience goes, not so beneficially. In use of the above explosive compounds made with cotton, as substitutes of gunpowder, care is to be observed that much

less by weight of the former than of the latter is to be employed to obtain a given result, and I believe, as a general rule, one part by weight of the compounds here described may be given as being equal in strength to (if not more powerful than) three parts by weight of Tower Proof gunpowder, and still less of the explosive compound should be used when it is substituted for gunpowder inferior in quality to Tower Proof. The explosive compound made by the use of cotton being in a fibrous state, it may be rammed into a piece of ordnance, a fowling-piece, or a musket, or it might be made up into cartridges, or, when slightly damp, it may be pressed into a mould adapted to the different calibres of fowling-pieces and pieces of ordnance, and on being dried it will retain its figure. I have also found that when placed in caps such as those now employed as percussion caps it might be discharged by impact. Explosive cotton, as herein described, and similar explosive compounds may also be used for many other purposes, for which gunpowder has hitherto been employed, and what I claim is the manufacture of explosive compounds from matters of vegetable origin, by means of nitric acid, or nitric acid and sulphuric acid."

It is interesting to note that the pulping of guncotton is mentioned in a patent of Tonkin,¹ in the year 1862. He describes the production of guncotton by nitration with mixed acid, and then goes on to say: "The cotton is to be washed in a continuous flow of water, and well agitated or stirred therein, till the water does not indicate the presence of any acid. The cotton has now to be pressed to free it from water as much as is practicable, and in order to ensure its being perfectly free from uncombined acid it is dipped in a very weak solution of potassium carbonate (1 oz. to 1 gall. water). The fibre is then taken in the wet state and converted into pulp in the same manner as is practised by paper-makers, by putting the fibre into a cylinder, having knives revolving rapidly, working close to fixed knives." Tonkin, however, makes no claim in his patent for the pulping of a guncotton, but only claims the addition of pulped guncotton to an explosive in the following proportions:—Nitrate of Soda, 65; Charcoal, 16; Sulphur, 16; and Guncotton Pulp, 3.

¹ *Improvements in the Manufacture of Gunpowder*. John Tonkin, Poole, Cornwall. English patent 320, 6th February 1862.

It was in the year 1865 that Mr F. A. Abel,¹ afterwards Sir Frederick Abel, took out a patent for *Improvements in the Preparation and Treatment of Guncotton*. This is historically of sufficient interest to have the more important points in the patent quoted in full, as follows:—"The method of treating the guncotton, which I prefer to employ in carrying my invention into practice, is as follows:—I first convert cotton-wool by the processes now well known into guncotton. For this purpose I prefer to use the cotton in the form of a loose roving. When the guncotton has been purified from acid by washing in running water and in very dilute alkali, I transfer it to a beating engine of the description commonly used in the manufacture of paper, where it is reduced to a pulp, which is then converted into solid masses, such as sheets, discs, cylinders, and other forms, either perforated or not, by any of the processes ordinarily employed for producing sheets, discs, cylinders, and other forms from paper pulp. A small quantity of gum or other binding material soluble in water may be mixed with the pulp. To obtain any required degree of density of the solid guncotton I subject the mass, whilst in a moist state, to the action of hydraulic or other presses, or of any other known arrangement of machinery for exerting the requisite pressure on the material. To produce a granular structure I either cut the sheets, discs, and other solid forms into small pieces of the required size, or I introduce the pulp containing water and a small quantity of the binding material into a vessel to which a vibrating motion is imparted, whereby the pulp is at once formed into granules of different sizes, which are subsequently sorted, if necessary. In the above processes, in place of water, other fluids, such as wood spirit, spirit of wine, ether, or mixtures of those liquids with or without some binding material soluble in the liquid, may be employed. Instead of forming the whole of the mass of guncotton into pulp as described, a portion of the same may be left in the original state, and be mixed with the pulp in such proportions that, when subjected to the requisite pressure, such combination will become a solid conglomerate mass of the requisite density. Such solid guncotton, whether formed of pulp only, or of pulp mixed with fibre, may also be coated or mixed with soluble guncotton,

¹ *Improvements in the Preparation and Treatment of Guncotton*. F. A. Abel, Royal Arsenal, Woolwich. English patent 1102, 20th April 1865.

known as collodion, applied in the form of solution. The solidified guncotton may also be formed of mixtures of guncotton of different composition, the properties of which are well known, that is to say, of guncotton which is soluble in mixtures of spirit of wine and ether, and in wood spirit, alone or mixed with spirit of wine, and of guncotton which is insoluble in those liquids, and the mixtures may be produced either by reducing both or only one of the varieties of guncotton to pulp, leaving the other in a fibrous state. Such mixtures may be converted into solid masses, either by the aid of pressure alone (that is, when one or both varieties is or are in the form of pulp), or by making the soluble guncotton present in the mixtures serve as a binding material by their treatment with the liquids above named, which act as solvents, in which case the mixtures may be consolidated with or without the aid of pressure."

CHAPTER VIII

LETTERS FROM BERZELIUS (1846), HALL AND SCHÖNBEIN
(1847), ON GUNCOTTON

IN 1846 Schönbein entered into negotiations with Messrs John Hall & Sons, Faversham (now associated with Messrs Curtis's & Harvey, Ltd.), who erected the first guncotton factory at Faversham. By a disastrous explosion on 14th July 1847 the factory was destroyed, with the loss of some twenty lives. The author is indebted to the kindness of Mr C. L. Watson-Smith, of Faversham, for the following historical letters on the subject of guncotton, and, in addition, some of the original intimations to miners and others on the sale and use of guncotton.

Letter from Professor J. Berzelius to Professor Schönbein.

STOCKHOLM, 18th November 1846.

SIR,—Your letter with which you honoured me under date of the 20th June came to my hands at the commencement of September only. Mr Merrian, who was the bearer of it, told me he had also to deliver a box of paper samples from you which he had left at Hamburgh, and he was unwilling to deliver the letter before he got the box, which had, however, been sent with his other things to Berlin, whither he intended to proceed in a few days. I requested him to deliver the box to our Minister at Berlin, which, however, he has not done, although he made an aerial excursion with the said Minister in Mr Green's balloon. As he stated to me at the same time that you had gone to England, I therefore delayed returning you my thanks for the information respecting the guncotton, until I should know where to address my letter to. I send the present to London at haphazard.

Accept my sincere congratulations on this as interesting as important discovery, the applicability of which you have at once endeavoured to show. Since Professor Otto of Brunswick

made known a method of preparing the guncotton, this discovery has perhaps occupied a greater number of inquisitive persons than any other chemical discovery ever did. I have likewise engaged in experiments upon it. I prepare it of equal parts in volume of concentrated sulphuric acid and the nitric acid of the shops at 1.45 sp. gr. I have found that it arises from the lignin and can be produced from the lignin of all vegetable substances, especially when we previously extract the encrusting substances by steeping it in a caustic maceration. I have prepared it from the *sphagnum palustre*, from tow, straw, and best of all from decayed and rotten wood, which, after removing the earthy particles by maceration, gives an excellent pulverulent gunpowder. I propose for its essential designation the term nitric lignin, since, being composed of these substances, it cannot be called guncotton. I have also attempted to prepare it from *cladonia rangiferena* and *letraria islandica*; but these contain a squelette which does not consist of lignin but of starch-like fibres and only produce nitric amyline (xyloidine).

The products of the combustion of nitric lignin, which are all gaseous, contain a gas which I consider to be cyanogen gas, which I certainly did not expect in them. I have not had time to investigate the precise elementary composition of this interesting combination, but I have dissolved them in a caustic alkali which is very easily done, and I have obtained from it nitric *glucine* acid, *apogline* acid, and other products of transformation not closely examined. I was quite disappointed in the hope that the lignin would again be generated in changing the nitric acid for water. You will greatly oblige me by communicating to me the results of your further investigations respecting the employment of nitric lignin as gunpowder.

With particular respect I have, etc.

Letter from Mr. Hall to Professor Schönbein, Bâle.

LONDON, 23 LOMBARD STREET, August 1847.

DEAR SIR,—The circumstances attending the late awful explosion of our guncotton establishment and the awful sacrifice of life connected with the destruction of so much property, have so overwhelmed us with trouble, and difficulty, that we

have hardly been able to settle our minds, so as to be able to make any detailed communication to you, on the subject.

Our Mr P. Brames Hall wrote to Mr Barron at Berlin and handed him the report of the inquest held at Faversham on Friday the 16th ultimo, as it appeared in the *Times* newspaper, and we understood from Mr Barron, that he enclosed this paper to you, but up to the time that he was here on the 11th instant he had not heard from you, neither have we had any letter from you on the subject. On the 9th instant the adjourned inquest was held and the jury came to the conclusion that Henry Toppin and others were killed by the explosion of a certain guncotton factory, but how that explosion arose no evidence appeared. Eighteen persons were killed by that explosion, ten only could be recognized, the remainder were literally blown to atoms, and scattered with the materials in every possible direction. One other person who inhaled the fumes of the acid, and who acted incautiously by not attending to medical advice, also died on the evening of the explosion, making nineteen persons. Of the survivors, fourteen in number, who suffered dreadfully by broken limbs, contusions, and being burnt by the acids, one has since died, and we fear one or two more will hardly recover. Some are maimed, and we are obliged by principles of sympathy to maintain them, and furnish medical advice and assistance.

We believe that arrangements that had been matured after many months of painful and hazardous personal attention, on the part of our Mr William Hall, worked out by practical and growing experience acquired by incessant application, for it must be remembered that any small essays of illustrating the mode of preparing, stoving and packing were perfectly futile, when applied to the production of the article in large quantities, where the control of temperature and the difficulty the men have in sustaining respiration with the drying and packing are brought into the account (without any special directions for large operations), are matters to which we must say we are indebted to our own experience and are all contingencies we have had to work out, and what we believe no house but ourselves would have had courage to encounter, but which have been thwarted with a destruction of life and property distressing to contemplate and alarming to the surrounding neighbourhood from the fear of any similar catastrophe.

This calamity, attended with all its trying and appalling

circumstances, has exceedingly embarrassed our position and has placed us in the situation of submitting to you the first moment we could get in the accounts, a balance-sheet showing the loss and the divisible third, which we place to your debit, in this painful matter. As much of the detail must have come to your knowledge by the public papers, you will, independent of the main facts, recognize what is the feeling of scientific men regarding the manufacture of the article on a large scale. We had made preparations and provided machinery to produce the article in large quantities, but as all scientific men agree that its principles are not even yet understood, no party can produce it without all those contingencies that endanger life and property, and that connected with the most determined opposition of public feeling and interested parties, preventing us getting it about the country, utterly precluding for the present any possibility of our concentrating any quantity in any magazines whatever of either public or private property.

For these reasons we now submit to you that the present agreement must be cancelled, and that we must be left entirely free and unfettered by any conditions to do the best we can, either with respect to any operations of our own in the re-erection and organization of our establishment for the manufacture of the article either now or hereafter, or in the granting of licences to companies or individuals under such plans, directions and instructions as we feel best adapted from the experience we have ourselves acquired, and this upon the *further* understanding that one-fourth of whatever profit may arise may be accorded to you, and three-fourths to ourselves. You may rest assured of the deep anxiety we have in working out this affair in the best way we can to recover some portion of the severe loss we have incurred, and that it remains with you to facilitate and promote our views in every possible way in your power, for we must confess to you that we should never have entered into any agreement or had anything to do with the matter had we not relied on your express declaration that the guncotton could be made for *tenpence sterling* per pound, a price assumed on fallacious data and wholly at variance with experience and facts. We intend to submit these accounts to Mr Barron, who will be able to trace every item and have any explanation that may be necessary for his satisfaction.

We are, etc.

Letter from Prof. C. F. Schönbein to Rev. J. A. Barron

BALE, 22nd October 1847.

MY DEAR BARRON,—The sad accident which occurred in Faversham some months ago, and of which Messrs Hall were kind enough to give me a short account some weeks back, induced me to write you some lines. Though I have already expressed to you my deep sorrow regarding that disastrous explosion, I cannot help returning once more to that melancholy subject and assuring you that no event in my life has ever produced such a deep and painful impression upon my mind as that to which I refer. You know that my humour is rather of a cheerful turn, but ever since I got that afflictive piece of intelligence my spirits have been saddened, and you may easily imagine how deeply I feel for Messrs Hall and in particular for him who had to witness the catastrophe himself and nearly fell a victim to it. It must have been the most trying moment in which a man can be placed in this life; and the killed and the wounded! I will stop here and confine myself to expressing my heartfelt wishes that it may please kind Providence to spare Messrs Hall a renewal of such hard trials.

Though I am rather disinclined to speak of matters of business on this occasion, still my standing to Messrs Hall renders it imperative to do so. I cannot deny that I was rather astonished at the extent of the devastations caused by the explosion, and infer from it that the quantity of exploded cotton must have been very considerable. You will be kind enough to inquire with Messrs Hall how large the quantity was. As to the cause of the explosion I feel quite sure that neither electricity nor self-combustion had anything to do with it, for the numerous experiments I have made with guncotton speak most decidedly against such a conjecture. My opinion is that the explosion took place in consequence of some inadvertence or other having occurred during the operation of drying the cotton. In other terms I think it very likely that some portion of guncotton was exposed to a degree of heat at which that substance is set on fire. Not knowing at all the manner in which the guncotton was dried in Faversham I should like very much to be made acquainted with the details of that subject and of the way in which the temperature of the drying stoves and rooms was ascertained.

Great as the misfortune of the explosion was, I trust it will not discourage men so full of spirit as Messrs Hall from resuming the manufacture of guncotton, for I feel quite confident that the preparation of that article is not connected with danger if the process of drying be carried on in a proper manner, *i.e.*, by a current of air moderately heated. As to the transport of guncotton I think I have proved beyond any shade of doubt that it is as safe as that of any other article. You know that I carried a comparatively large quantity of guncotton in my trunk last year and that I made a journey of at least 1200 miles on railroads, stage coaches, steamboats, etc., where my luggage was very often roughly treated, and not the slightest accident happened to my cotton box. A fairer and a more decisive trial cannot be made to show the groundlessness of the fear that guncotton might explode during its transport.

Pray present my best compliments to Mrs Barron and Messrs Hall and believe me, yours, etc.

The following instructions and notifications with respect to guncotton are also historically interesting:—

London Gunpowder Office, 23 Lombard Street, 19th November 1846.

GUNCOTTON

Very numerous applications having been made to us for a supply of Patent Guncotton (for sporting and blasting purposes), we deem it necessary to inform the public that extensive preparations are in progress for the manufacture of this article, which will shortly be completed, when due notice will be given to gunmakers and mine agents, who may be desirous of obtaining a supply. Persons detected in making, using, or vending any imitation of the patent article, will be proceeded against on all occasions. JOHN HALL & SON, Patentees of Professor Schönbein's Guncotton for England, Scotland, Ireland and the British Colonies.

Directions for using Schönbein's Patent Guncotton, applicable for blasting every description of rock and mineral.

It is recommended that safety fuse should be used, and inserted into the cartridge to the extent of about two inches,

and tied fast to the neck of the cartridge with a piece of string. There is a black dot at one end of the cartridge to show where the fuse is to be inserted.

The hole to be tamped should be made sufficiently large in diameter, that the cartridge may reach the bottom without there being any occasion to force the same down. The hole should be made as dry as possible before the cartridge is inserted. When the cartridge is down to the bottom of the hole, put into the hole a handful of dry sand or clay, so as to cover the top of the cartridge to the depth of one or two inches, then proceed to ram or stem down, precisely as in the case of blasting with gunpowder. The fuse being cut off to the required length, according to circumstances, all is ready for firing. Where there is an absolute necessity for using the guncotton in a loose state, a wooden rammer only is to be used.

To mine and colliery proprietors, slate quarry owners, railway contractors, ironmongers, dealers in gunpowder, and others.

Messrs John Hall & Son, the patentees and sole manufacturers of Schönbein's patent guncotton, respectfully state that they are now prepared to supply the patent guncotton (compressed for convenience of carriage), in round and square paper cases of four ounces each, packed in boxes containing 50 and 100 cases each, at the price of three shillings per pound, for ready money. Also in tubes or cartridges of 1, $1\frac{1}{8}$, $1\frac{1}{4}$, and $1\frac{1}{2}$ inches diameter, containing 2, 4, 6, and 8 ounces each, at the additional charge of 1, $1\frac{1}{2}$, 2, and $2\frac{1}{2}$ pence, each tube or cartridge. For blasting in slate quarries, paper tubes will be supplied three feet in length, containing one ounce of the patent guncotton per foot. Four ounces of guncotton are equal in power to 24 ounces of blasting gunpowder, as proved in mortars, similar to those used by the Board of Ordnance, for the proof of gunpowder.

CHAPTER IX

THE BRITISH ASSOCIATION COMMITTEE ON GUNCOTTON (1863)

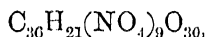
AFTER the discovery of guncotton by Schönbein in 1846, the thoughts of many were directed to its application to warlike purposes. Many trials and experiments were made, especially by the French Government; but such serious difficulties and objections presented themselves, that the idea seemed to have been abandoned in every country but one. That country was Austria. From time to time accounts reached England of its partial adoption in the Austrian Service, though no explanation was afforded of the mode in which the difficulties had been overcome, or of the extent to which these attempts had been successful.

This was the state of the case when a Committee was appointed in 1862 by the British Association for the Advancement of Science to report upon the matter. The Committee contained some ten of the best known scientists of that time. It was put in possession of the fullest information on the subject, mainly from two sources. (1) A report by Abel, by permission of the Secretary of State for War, containing the information given by the Austrian Government to the English Government, of the method of manufacture in the Austrian Factory. (2) General von Lenk, on the invitation of the Committee, and by permission of the Emperor of Austria, paid a visit to England, with the object of answering any inquiries the Committee might make, and explaining his system of manufacture thoroughly, and for this purpose he brought over drawings and samples from the Imperial Factory. In addition to these principal sources of information, special services were also rendered by two of the members of the Committee. Frankland was able to corroborate, by his own experiments, most of the statements made in the earlier communications of Abel. Whitworth made experiments on the application of guncotton in mines, and sent over to Austria rifles and ammunition to be experimented with by von Lenk, with a view of obtaining

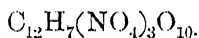
results, which he communicated to the Committee. The following are the conclusions arrived at by the Committee after their investigation.

Chemical Considerations.—Under this head are included the manufacture of the guncotton itself, and the answers to such inquiries as those which refer to its liability, or non-liability, to deterioration on keeping; the possibility of its spontaneous decomposition; and the nature and effects of the products into which it is resolved on explosion.

As to the chemical nature of the material itself, Baron von Lenk's guncotton differs from the guncotton generally made, in its complete conversion into a uniform chemical compound. It is well known to chemists that when cotton is treated with mixtures of strong nitric and sulphuric acids, compounds may be obtained varying considerably in composition, though they all contain the elements of the nitric acid, and are all explosive. The most complete combination, or product of substitution, is that described by Hadow as



which is identical with that termed by the Austrian chemists trinitrocellulose—



This is of no use whatever for making collodion, but it is Baron von Lenk's guncotton, and he secures its production by several precautions. Of these the most important are:

(1) The cleansing and perfect desiccation of the cotton, as a preliminary to its immersion in the acids.

(2) The employment of the strongest acids obtainable in commerce.

(3) The steeping of the cotton in a fresh strong mixture of acids, after its first immersion and partial conversion into guncotton.

(4) The continuance of the steeping for forty-eight hours.

(5) The thorough purification of the guncotton so produced, from every trace of free acid. This is secured by its being washed in a stream of water for several weeks. Subsequently a weak solution of potash may be used, but this is not essential.

The prolonged continuance of these processes appears at first sight superfluous, but it is really essential; for each cotton fibre is a long narrow tube, often twisted and even doubled up, and the acid has first to penetrate into the very furthest depths

of these tubes, and afterwards has to be soaked out of them. Hence the necessity of time. It seems to have been mainly from want of these precautions that the guncotton experimented on by the French Commission gave irregular and unsatisfactory results.

From the evidence before the Committee, it appears that this highest nitro-compound, when thoroughly free from acid, is not liable to some of the objections which have been urged against the mixture of compounds which has been usually employed for experiments on guncotton.

These advantages may be classed as follows:—

(1) It is of uniform composition, and thus the force of the gases generated on explosion may be accurately estimated.

(2) It will not ignite till raised to a temperature of at least 136° C., a heat which does not occur unless artificially produced by means which would render gunpowder itself liable to ignition.

(3) It is almost absolutely free from ash when exploded in a confined space.

(4) It has a very marked superiority in stability over other forms of guncotton. It has been kept unaltered for fifteen years, and is not liable to that slow spontaneous decomposition which is known to render lower products worthless after a short time. Yet there are still some reasons for suspecting that even the guncotton produced at the Imperial Works suffers some gradual deterioration, especially when exposed to sunlight.

There is one part of the process not yet alluded to, and the value of which is more open to doubt, namely, the treatment of the guncotton with a solution of silicate of potash, commonly called water-glass. Abel and the Austrian chemists think lightly of it; but Baron von Lenk considers that the amount of silica set free on the cotton by the carbonic acid of the atmosphere is really of service in retarding the combustion. He adds that some of the guncotton made at the Austrian Imperial Works has not been silicated at all, and some but imperfectly; but when the process has been thoroughly performed, he finds that the guncotton has increased permanently about 3 per cent. in weight. A piece of one of the samples left by the General was indeed found to contain 2.33 per cent. of mineral matter, consisting chiefly of silica.

Much apprehension has been felt about the effect of the

gases produced by the explosion of guncotton. It has been stated that both nitrous fumes and prussic acid are among these gases, and that the one would corrode the gun, and the other poison the artilleryman. Now, though it is true that from some kinds of guncotton, or by some methods of decomposition, one or both of these gases may be produced, the results of the explosion of the Austrian guncotton, without access of air, are found by Karolyi to contain neither of these, but to consist of nitrogen, carbonic acid, carbonic oxide, water, and a little hydrogen and light carburetted hydrogen. These are comparatively innocuous; and it is distinctly in evidence that, practically, the gun is less injured by repeated charges of guncotton than of gunpowder, and that the men in casemates suffer less from its fumes. The importance of this latter property in a fortress, or a ship, will be at once apparent.

It seems a disadvantage of this material, as compared with gunpowder, that it explodes at a lower temperature, possibly at 136° C.; but against the greater liability to accident arising from this cause may be set the greatly diminished risk of explosion during the process of manufacture, since the guncotton is always immersed in liquid, except in the final drying; and that may be performed, if desirable, at the ordinary temperature of the air. Again, if it should be considered advisable at any time, it may be stored in water, and only dried in small quantities when required for use.

The fact that guncotton is not injured by damp like gunpowder, is indeed one of its recommendations. It is not even so liable to absorb moisture from the atmosphere, 2 per cent. being the usual amount of hygroscopic moisture found in it; and should that quantity be increased through any extraordinary conditions of the air, the guncotton speedily parts with its excess of moisture when the air returns to its ordinary state of dryness.

But a still more important chemical advantage which guncotton possesses, arises from its being perfectly resolved into gases on explosion, so that there is no smoke to obscure the sight of the soldier who is firing, or to point out his position to the enemy; and no residue left in the gun to be got rid of before another charge can be introduced.

Practical Applications.—Guncotton is used for artillery in the form of thread or spun yarn. In this simple form it will

conduct combustion slowly in the open air at a rate of not more than 1 foot per second. This thread is woven into a texture or circular web. These webs are made of various diameters; and it is from these webs that common rifle cartridges are made, merely by cutting them into the proper lengths, and enclosing them in stiff cylinders of pasteboard, which form the cartridges. In this shape its combustion in the open air takes place at a speed of 10 feet per second. In these cylindrical webs it is also used to fill explosive shells, as it can be conveniently employed in this shape to pass in through the neck of the shell. Guncotton thread is spun into ropes in the usual way, up to 2 inches in diameter, hollow in the centre. This is the form used for blasting and mining purposes; it combines great density with speedy explosion, and in this form it is conveniently coiled in casks and stowed in boxes. The guncotton yarn is used directly to form cartridges for large guns, by being wound round a bobbin, so as to form a spindle like that used in spinning mills. The bobbin is a hollow tube of paper or wood. The object of the wooden rod is to secure, in all cases, the necessary length of chamber in the gun required for the most effective explosion. The circular guncotton web is enclosed in tubes of indiarubber cloth to form a match-line, in which form it is most convenient, and travels with speed and certainty.

Conveyance and Storage of Guncotton.—It results from the foregoing facts that, in artillery, 1 lb. of guncotton produces the effect of more than 3 lb. of gunpowder. This is a material advantage, whether it be carried by men, by horses, or in wagons. It may be placed in store and preserved with great safety. The danger from explosion does not arise until it is confined, as it simply burns intensely in the open air. It may become damp, and even perfectly wet without injury, and may be dried by mere exposure to the air. This is of great value in ships of war; and in case of danger from fire, the magazine may be submerged without injury.

Practical Use in Artillery.—It is easy to gather from the foregoing general facts, how guncotton keeps the gun clean, and requires less windage, and therefore performs much better in continuous firing. In gunpowder there is 68 per cent. of refuse, or the matter of fouling. In guncotton there is no residuum, and therefore no fouling.

Experiments made by the Austrian Committee proved that 100 rounds could be fired with guncotton against 30 rounds with gunpowder.

In firing ordnance with guncotton, the gun does not heat to any important extent. Experiments showed that 100 rounds were fired with a 6-pounder in 34 minutes, and the gun was raised by guncotton to only 50° C., whilst 100 rounds with gunpowder took 100 minutes, and raised the temperature to such a degree that water was instantly evaporated. The firing with the gunpowder was therefore discontinued; but the rapid firing with the guncotton was continued up to 180 rounds without any inconvenience. The absence of fouling allows all the mechanism of a gun to have more exactness than where allowance is made for fouling. The absence of smoke promotes rapid firing and exact aim.

The fact of smaller recoil from a gun charged with guncotton is established by direct experiment; its value is two-thirds of the recoil from gunpowder—the propulsive effect being equal. To understand this may not be easy. The waste of the solids of gunpowder accounts for one part of the saving, as in 100 lb. of gunpowder, 68 lb. have to be projected in addition to the shot, and at much higher speed. General von Lenk attributes the remainder to the different law of combustion; but the fact is established.

Advantage in Weight of Gun.—The fact of the recoil being less, in the ratio of 2:3, enables a less weight of gun to be employed as well as a shorter gun, without the disadvantage to practice arising from lightness of gun.

Endurance of Gun.—Bronze and cast-iron guns have been fired 1000 rounds without in the least affecting the endurance of the gun.

Under Water.—Two tiers of piles 10 inches thick, in water 13 feet deep, with stones between them, were blown up by a barrel of 100 lb. of guncotton placed 3 feet from the face, and 8 feet under water. It made a clean sweep through a radius of 15 feet, and raised the water 200 feet. In Venice, a barrel of 400 lb. placed near a sloop in 10 feet of water at 18 feet distance shattered it to pieces and threw the fragments to a height of 400 feet.

The Committee desire to put upon record their conviction that the subject has neither chemically nor mechanically re-

ceived the thorough investigation which it deserves. There remain many exact measurements still to be made, and many important data to be obtained. The phenomena attending the explosion of both guncotton and gunpowder have to be investigated, both as to the temperatures generated in the act of explosion, and the nature of the compounds which result from them under circumstances strictly analogous to those which occur in artillery practice; and until these are accurately ascertained, it is impossible to reconcile the apparent contradictions between the mechanical phenomena which result from the employment of guncotton gases and gunpowder gases, when employed to do the same kind of mechanical work.

CHAPTER X

THE MANUFACTURE OF GUNCOTTON IN AUSTRIA (1863)

THE Committee of the British Association had before them details of the method of manufacture of guncotton in Austria, and also submitted to Baron von Lenk a great number of questions, to which he replied in detail. In addition, there was also a report, by three of the foremost Austrian chemists of that time, upon von Lenk's guncotton, and the system of manufacture. Extracts from all these sources have been embodied in the present paper.

System of Manufacture of Guncotton as carried on in the Imperial Austrian Establishment.

(1) The cotton employed is of superior quality, tolerably free from seed; it is carded loosely, twisted, and made up into skeins before conversion. The strands of the cotton composing the skeins are of two sizes—the larger being intended for cannon cartridges, and the other for small-arm cartridges and bursters.

(2) *Preparatory Treatment of the Cotton.*—The cotton, made up into skeins weighing about 3 ounces each, is washed in a solution of pure carbonate of potash of a sp. gr. of 1.02, being immersed in the boiling solution for a short time. Upon removal from the alkaline liquid, the skeins are placed in a centrifugal machine, by which the greater portion of the liquid is separated. The skeins are now washed in clear running water, either by allowing them to remain in it for three or four hours, or else by washing each skein by hand for a few minutes. They are then again worked in a centrifugal machine and afterwards dried—in summer by the rays of the sun, but during winter in a drying-house heated by air-pipes to between 30° and 38° C.; the latter plan usually takes four or five days.

(3) *Production of the Guncotton.*—The nitric acid employed has a sp. gr. of 1.53, and the sulphuric acid a sp. gr. of 1.82. They are mixed in the proportion of three parts by weight of sulphuric acid to one part of nitric acid.

Two skeins (about 6 ounces) of the cotton are immersed at

one time in the mixed acids, and moved about for a few moments with iron paddles. They are then raised upon a grating above the level of the acids and submitted to gentle pressure; thence they are transferred to covered stone jars, each of which receives six skeins of known weight. The jars are then weighed, some of the mixed acids being added if necessary, to bring the proportion of acids up to $10\frac{1}{2}$ lb. to 1 lb. of cotton.

The jars are set aside for forty-eight hours in a cool place; in summer they should be placed in cold water. When that period has elapsed, the acid is separated from the cotton, as far as possible, by means of a centrifugal machine, as before described. The men working the machine are protected from the fumes of the acids by a wooden partition. The acids removed from the cotton are not used again in the preparation of guncotton.

The skeins of guncotton are at once removed from the centrifugal machine to perforated receptacles, which are immersed in a stream, where they are allowed to remain at least three weeks. Each skein is afterwards separately rinsed in the stream to remove mechanical impurities, and the water is then separated by the centrifugal machine.

The guncotton is next submitted to treatment with a solution of carbonate of potash, as in the preliminary process, and again washed after the alkaline liquid has been expressed. When the skeins have been allowed to dry tolerably by simple exposure to the air, they are placed in a large wooden tub containing a solution of silicate of soda, the temperature of which is about 15° C. This solution should have a sp. gr. of 1.072, and is prepared as required from a solution of sp. gr. 1.216. The cotton remains one hour in the solution of silicate of soda, which is supposed to exercise two functions:—

- (a) That of protecting the cotton by acting as a varnish upon the fibres.
- (b) That of retarding its combustion.

Upon removal of the guncotton from the bath of water-glass, the liquid is partly expressed by hand, and afterwards more fully by means of the centrifugal machine. The skeins must then be thoroughly dried. They are afterwards immersed in running water for five or six hours, and each skein is subsequently washed by hand. The water having been extracted by the centrifugal machine, the guncotton is removed to the

drying-house, where it remains eight or ten days. Its manufacture is then completed. The guncotton is packed in ordinary deal boxes lined with paper, and kept in dry magazines until required to be made into cartridges, etc. Well-organized arrangements are employed for mixing the sulphuric and nitric acids, immersing the cotton, and for conducting the various other operations connected with the manufacture.

Abel found in the Austrian guncotton, after drying *in vacuo* over sulphuric acid, a moisture of about 2 per cent. He further analyzed the samples according to the method devised by Hadow, which consisted in digesting weighed quantities of the guncotton in the cold for 24 hours, in an alcoholic solution of potassium hydrogen sulphide, and the reduced cotton, thus produced, was thoroughly washed and dried. The products so produced were proved to be free from nitrogen compounds by igniting portions with potassium hydroxide, when no indication of the existence of nitrogen in the specimens was obtained. Theoretically, trinitrocellulose should give 54.54 per cent. of regenerated cotton. Abel's results with the Austrian guncotton were as follows:—

54.97, 55.13, 55.07 and 55.20 per cent.

The ash in the various guncottons varied from 0.42 per cent. to 1.9 per cent. Von Lenk considered that impregnation of the guncotton with soluble glass was very advantageous. According to his view, it closed the pores of the guncotton fibre, by precipitating silica within them, and the velocity of explosion of the guncotton was thus retarded; and further, any trace of acid remaining would be neutralized by combination with the sodium carbonate liberated from the soluble glass.

Abel could not find that any proportion of silica of any moment remained, after carrying out the process as described by von Lenk, *i.e.*, washing in running water for 5 or 6 hours, and the subsequent rinsing of each skein after the treatment with silicate of soda. Von Lenk also considered it desirable to keep the fibres of the guncotton soft, in order to guard against the contingency of explosion from very violent friction. This was effected by dipping the material, previous to final drying, in a soap solution, the excess being afterwards squeezed out, and the guncotton dried.

The Austrian chemists pointed out the following differences between the French guncotton and that of von Lenk. "Ac-

according to the method pursued by the French Commission, the raw cotton was immersed in the acid mixture for one hour. Baron von Lenk leaves his cotton forty-eight hours in the acid bath. The French cotton was afterwards dipped in running water for an hour or an hour and a half. Baron von Lenk's guncotton lies four, six, or eight weeks in a stream. The French cotton had, after washing, so much free acid left, that carbonate of potash was neutralized by contact with it, and after long use became acid. Baron von Lenk's cotton is so freed from acid by long immersion, that a 2 per cent. solution of potash, in which 2 cwt. of guncotton had been boiled, had lost none of its alkaline properties, and hence the guncotton was completely free from acids. The French guncotton, having been prepared in so different a manner, must necessarily have had a different composition from that of Baron von Lenk's; hence it is clear that the French experimental results cannot, without considerable reserve, be accepted as precedents."

They further go on to say: "The history of guncotton, as chronicled by chemists and artillerymen, short though the history be, is so full of records of explosion under unexpected circumstances, that an unbiased mind can hardly fail to be impressed with the belief that, amongst the ordinary conditions of military practice, there may be some competent to induce the spontaneous combustion of this material. Nevertheless the experience of Baron von Lenk, acquired during a period extending over more than ten years, is more pregnant with reliable testimony than can be found in the entire remaining history of this material. The manufacture of guncotton in Hirtenberg consists of a number of perfectly harmless operations; and it is remarkable that, contrary to what happens with gunpowder, if fire be not actually applied, explosion is impossible. All operations are so arranged that the material acted upon is in a moist or wet condition—hence not explosive. Drying takes place in a capacious building, open to the air on every side. The last process of drying is carried out in the drying-chamber, where it is effected by a stove situated on the outside, distributing its heat to the building by earthenware pipes—drying being thus ensured through a gentle warmth. The guncotton next goes either into a magazine to be packed away in chests, or is at once prepared for ammunition. In this magazine, Hirtenberg cotton has been stored for a period of twelve years, and not a single

instance of explosion has taken place. How many powder-mills have exploded in that time? In Prussia, however, a drying-chamber has lately blown up; but they have worked for eight years with guncotton, and not a single explosion has occurred except the last-named. In the Prussian drying-chamber referred to, a stove with iron smoke-pipe was used—a sufficient explanation of the misfortune. During twelve years we have prepared guncotton at Hirtenberg for ammunition—that is, for yarns, spun ropes, and threads twisted and woven. One single case of explosion has occurred in the course of Baron von Lenk's manufacture, the result of improper speed of working the spinning machinery. Now, the circumstances hardly need be insisted on, that gunpowder as well as guncotton can be exploded by friction. Guncotton has now been used for military purposes for more than twelve years; it has also been employed for mining and blasting. It has been subjected to every variety of transport. Packed in black wooden chests, it has been exposed to sunshine for months together—all this without one single accident. In the face of such testimony, it cannot be said that guncotton manifests any tendency to explode spontaneously."

CHAPTER XI

THE MANUFACTURE OF GUNCOTTON AT WALTHAM ABBEY (1863)

ABEL communicated to the Committee at the British Association, the details of his method of manufacture at Waltham Abbey, from which the following extracts are taken:—Very considerable difficulties were experienced in procuring the small quantity of cotton (two or three cwts.) required for these experiments, in a condition resembling sufficiently closely that employed at Hirtenberg, as its production in the form of the thick and the thin loose rovings or yarn, necessitated some deviation from the ordinary method of spinning, which it was difficult to induce manufacturers to attempt without the promise of an extensive order. Eventually I succeeded in obtaining the requisite quantity of coarse and fine yarn or roving, resembling closely in character, and quality of cotton, the specimens obtained from Hirtenberg. The acids were readily obtained at moderate prices—the sulphuric acid having a sp. gr. of 1·84, and that of the nitric acid (a light amber-coloured acid) being 1·52. The apparatus and implements employed, and the modes of conducting the various operations, were, as closely as practicable, in accordance with those in use in Hirtenberg, a slight deviation only, in the form or material of some of the implements, being adopted where it was decidedly advantageous and could not in any way influence the nature of the results. The following is an account of the details of manufacture:—

Preparation of the Cotton.—The cotton was made up into skeins, those of the stout yarn weighing from four to six ounces each, and those of the fine yarn from three to four ounces. It was then boiled for about 15 minutes in a dilute solution of potassium carbonate (sp. gr. 1·02) and transferred thence to a centrifugal machine. The cotton was then washed thoroughly, first by hand in a large tank, and afterwards by submersion in a stream for forty-eight hours. The water was separated from

the skeins by the aid of the centrifugal machine, and the purified cotton was then dried. Although the cotton was of good quality and very fairly cleaned from seed (being quite equal in these respects to the Austrian samples), it was found to sustain a loss of about 5 per cent. by the treatment with alkali and by washing. The potash solution in which it was boiled acquired a coffee colour. Portions of seed were still retained by the purified cotton, which were subsequently dissolved out perfectly by the acids.

Preparation of the Acids.—The proportions of acids (three parts by weight, or 2.45 by volume, of sulphuric acid to one part of nitric acid) were weighed off and transferred to barrel-shaped stoneware vessels provided with taps, two of these receiving the sulphuric acid and a third the nitric acid. The barrels were so arranged upon a suitable table that the acids could be delivered from the taps into a deep and very capacious stoneware vessel, fitted with an iron lid with suitable apertures and a tap; this vessel was raised from the ground sufficiently to allow of the acids being transferred from it to well-stoppered stoneware bottles. While the acids were flowing slowly and uniformly from the barrels into the covered mixing-vessel, the resulting mixture was kept continuously stirred by means of a large iron paddle, and after they had been entirely transferred (which occupied about ten minutes), the stirring was continued for about twenty minutes before the mixture was drawn off into the bottles. The product of this operation had a sp. gr. of 1.82. The acid, thus prepared, was set aside in a cool place, and never employed until at least twenty-four hours after the mixture had been made.

Treatment of the Cotton with the Mixed Acids.—About twelve hours before immersion in the acids, the skeins to be operated upon at one time (which had previously been dried in the air) were suspended in a drying-chamber, at not less than 49° C. They were then transferred, while in the chamber, to stoneware jars with tightly-closing lids, and were allowed to become perfectly cold in these before submission to treatment with acid. The vessels which were found most suitable for use in treating the cotton with the acid were large and rather deep stoneware pans. One, provided with an iron lid, contained the quantity of mixed acids required for the treatment of a certain number of skeins; a second, which was fitted with a perforated ledge

of iron, and was surrounded by cold water, served for the treatment of the cotton, which was conducted as follows:—A portion of the acid having been transferred to the second pan, two skeins were thoroughly immersed in it, and stirred about for two or three minutes; when saturated with acid they were raised upon the shelf and pressed together with the paddle, so as to allow the superfluous acid to flow off; the quantity of acid absorbed by these skeins was replaced in the pan by an addition of fresh acid, and further skeins were immersed, those which had drained being transferred to a jar while the freshly immersed ones were soaking. In this way the operation of immersion was continued until the whole of the skeins to be treated at one time had been transferred to the jars, six of the large yarn or nine of the fine being introduced into one of these. The skeins were pressed down in the jars by means of the paddle, and sufficient acid was added just to cover the cotton completely. The jars were then closed and placed in vessels containing water, in a cool building, where they remained for forty-eight hours. It was found an important precaution to keep the vessel in which the cotton was first immersed surrounded with water, especially in the warm season during which these experiments have been conducted, as the evolution of heat during the first action of the acids upon the cotton is considerable. The contents of the jars to which the guncotton was transferred, were not found to become heated to any important extent, even when not surrounded by water. The proportion of acid to cotton said to be contained in the jars, as the process is carried out at Hirtenberg, is that of ten to one; but it was found necessary, in order to cover the cotton completely as directed, to employ at least fifteen parts of acid to one of cotton. This proportion would doubtless be much diminished if means were employed for compressing the cotton in the jars more highly than was the case in these experiments. The precaution of adding a fresh supply of acids to that which remains in the immersing vessel after the withdrawal of each quantity of cotton treated, was proved by experiment to be of the greatest importance in securing the uniformity of the product. In one of the first operations, no fresh quantity of acid was added before immersing the skeins treated last. In other respects these skeins were submitted to precisely the same treatment as the remainder (*i.e.* an additional quantity of acid was added to

them in the jar, they were allowed to remain for forty-eight hours, etc.) When examined synthetically, they furnished at least one-half per cent. more cotton than the skeins first treated in the same operation; and when fired in the proof-mortar, a decidedly lower range was obtained with the cotton last treated.

Purification of the Guncotton.—At the expiration of forty-eight hours the jars were conveyed to a centrifugal machine. The machine employed at Hirtenberg for this purpose is made of copper, the one used by me was constructed entirely of iron, the sides of the revolving cylinder consisting of coarse iron-wire gauze, rendered sufficiently rigid by an iron framework. After each operation the machine was washed out with an abundant supply of water, and thus the corrosive action of the acids upon it has really been very trifling. The skeins were rapidly transferred, by means of an iron hook, to the centrifugal machine. Within ten minutes the acid was so far separated from the cotton that the skeins were only damp. Some precautions were necessary in effecting the first transfer to water of the skeins, with acid still clinging to them. If they were simply thrown into water, so that the latter would penetrate them only gradually, the heat resulting from the union of the free acids and the water immediately established a violent action of the nitric acid upon the cotton, quantities of nitrous vapours being disengaged. At Hirtenberg the guncotton, when taken from the machine, is quickly placed under a small cascade, where its saturation with water is effected with very great rapidity. As this arrangement was not attainable at Waltham Abbey, the skeins, directly they were removed from the machine, were plunged singly, as rapidly as possible, and moved about violently, in a large body of water. They were then washed by hand in a stream until no acid taste whatever was perceptible in the cotton, and were afterwards immersed in the stream for a period of not less than forty-eight hours. For this purpose they were arranged in rows upon poles fixed in frames, which were so placed in the water that the skeins were in a vertical position, the water circulating among them freely. The current of the stream used at Waltham Abbey (at the only available place for these experiments) was not so rapid as could have been desired, and the dryness of the season had rendered it unusually sluggish; still it was sufficient to afford a continual change of the water surrounding the cotton. The character of this water is by no means such as to

render it specially fitted for the purification of the guncotton. The bed of the stream is always thickly covered with luxuriant vegetable growth, and the water itself is consequently so highly charged with vegetable matter, that, although light was excluded as far as possible from the cotton during its immersion, the skeins became covered in many places, within a few days, by vegetable growth, which in time attached itself so firmly to the cotton as to be very difficult of removal by hand-washing. The system of purification, as carried on at Hirtenberg, differs very considerably from that described in General von Lenk's process as patented in this country. At the above-named establishment, the guncotton is in the first instance left in the stream for three weeks and upwards; it is afterwards washed in a dilute solution of potassium carbonate, again washed in water, dried, and then treated with a solution of soluble glass. After this treatment it is dried, washed for six hours in the stream, and finally by hand. In the patented process, it is directed that the guncotton, in the first instance, should be immersed in running water for forty-eight hours and upwards; it is not submitted to any treatment with potassium carbonate, but is boiled, after the first washing, in a weak solution of soluble glass, and on its removal from this, without any intermediate desiccation, it is immersed in the stream for about six days. The process of purification which I adopted differed from that in use at Hirtenberg only in the postponement of the long-continued washing until after treatment of the guncotton with alkali. At the expiration of forty-eight hours the skeins were removed from the stream, centrifugalled, and then boiled for a few minutes in a solution of potassium carbonate of sp. gr. 1.02. Having been returned to the centrifugal machine, they were again placed in the washing-frames and left in the stream for a period of fourteen to eighteen days. On subsequent removal from the stream, each skein was washed by hand, to separate mechanical impurities, and one half of each quantity of guncotton prepared was finally left in soak in distilled water for some hours. The guncotton thus finally purified was dried in the open air.

The Treatment of the Purified Guncotton with Soluble Glass.—In General von Lenk's process, as described in the English patent, the soluble glass is applied, as already stated, to the guncotton, which, after the removal from the acids, has undergone no

further treatment than an immersion in running water for forty-eight hours or thereabouts; when removed from the bath of silicate, the guncotton is not dried but is at once immersed for a period of six days in running water. It is at once obvious that this treatment cannot exert any effect upon the cotton, beyond possibly the neutralization of a minute trace of free acid still retained by it after the first washing. That the treatment with soluble glass is not intended to exert any other than a purifying effect upon the guncotton, appears also to have been understood by Professors Redtenbacher, Schrotter, and Schneider, in their inquiry into Baron von Lenk's system of manufacture; for the only allusion which they make in their joint report to this point is as follows: "The treatment with soluble glass has no influence on Baron von Lenk's guncotton, it being previously free from acids." In order to test the system of manufacture as carried on at Hirtenberg, it was determined to submit one half of each quantity of guncotton produced in one operation to the treatment with soluble glass, the other half being dried, as a finished product, after the immersion in distilled water. The first portion was soaked for one hour in a boiling 2 per cent. solution of the silicate. After being centrifugalled the guncotton still retained about 80 per cent. of the solution, which, by evaporation, left therefore about 8 per cent. of soluble glass in the material. The skeins were thoroughly dried in air, and then immersed in the stream for about forty-eight hours. A longer period of immersion was adopted than in use at Hirtenberg, on account of the comparatively sluggish current of the river. The skeins were finally washed by hand and dried, this operation completing the manufacture of the guncotton. The ash of a "silicated" product was 1.85 per cent.; that of the non-treated 1.45 per cent. The proportion of silica left in the guncotton was greater than that found in the Austrian specimens; but the portion not treated with soluble glass also contained a very notable amount of silica, derived from suspended matter in the water. Artificial heat was not employed in drying any portion of the purified guncotton. This operation was accomplished by suspending the skeins during the day upon lines in the open air, or in a well-ventilated shed in wet weather and at night.

CHAPTER XII

ABEL ON GUNCOTTON (1866)

THE first of Abel's classical researches on guncotton was communicated to the Royal Society in 1866.¹

He deals, first of all, with the work which had been done both in Great Britain and on the Continent on the composition of guncotton, and gives the various formulæ proposed for this body.

His own work first devotes attention to the moisture absorbed by guncotton. He found it to be very uniform; the average proportion being about 2 per cent. The average amount of ash was found to be about 1 per cent. The solubility of guncotton in a mixture of ether and alcohol is treated at considerable length, and the following was his method of analysis. The weighed guncotton (between 2 and 3 grms.) was packed closely into a tube of about 12 mm. diameter and constricted to a fine opening at the lower extremity. The mixture of ether and alcohol which was poured on to the guncotton in the tube filtered through it very slowly. When the filtrate furnished what appeared an unimportant quantity of residue, the guncotton in the tube was dried, and its loss in weight determined. Upon examining the samples of guncotton thus treated, they were found, however, still to contain matter soluble in the ethereal mixture, and it was evident that by this mode of treatment, either the soluble matter could not be separated from the insoluble fibre, or only the most readily soluble portions (which furnish a tolerably limpid solution) were carried through by the liquid; while those less easily dissolved, and which were, indeed, more glutenized than actually dissolved, remained in the tube. A different mode of operating was therefore resorted to. From 8 to 10 grms. of the guncotton were digested in a stoppered bottle for from thirty to fifty hours (according to the apparent extent of action of the solvent) with from 60 to 100 cc. of ethereal mixture. At the expiration of this digestion the con-

¹ *Trans. Roy. Soc.* (1866), 269-308.

tents of the bottle were agitated slightly, a small portion of the guncotton was removed and placed as a plug in the apex of a funnel, through which the liquid was filtered into an evaporating dish. The guncotton was then transferred to a suitable instrument, placed over the funnel, and the liquid expressed; it was afterwards returned to the bottle, in which it was digested for a second (and sometimes a third) similar period with fresh solvent, the washings of the funnel, etc., being returned to the bottle. When the guncotton had been two or three times digested and expressed, it was washed upon the funnel. The liquid thus obtained never contained more than two or three minute fibres of the guncotton; it was generally of a very pale straw colour, and slightly opalescent. When evaporated nearly to dryness it became gelatinous, and gradually dried to a yellowish substance of somewhat resinous appearance. The examination of twenty samples of guncotton manufactured at Waltham Abbey from 1863 to 1865 gave as the lowest result 1.3 per cent., as the highest result 2.6 per cent., and a mean of 1.99 per cent. On prolonged immersion of cellulose in the mixed acids the following percentage solubilities in ether-alcohol were obtained. Twenty-four hours, 1.99; forty-eight hours, 2.4; seventy-two hours, 2.3.

Somewhat higher results were obtained by submitting the material to long continued agitation with ether and alcohol, and repeating the digestion and agitation several times with fresh solvent; but the guncotton became so disintegrated by this treatment, that it was very difficult to filter the liquid so as to obtain it free from fibres; it was moreover found that a considerable proportion of the finely divided mineral matter attached to the guncotton became suspended in the liquid and could not be separated. Repeated experiments showed that, after the second digestion of Waltham Abbey guncotton, there were only very small quantities of soluble matter extracted, which it appeared almost impossible to remove perfectly by this mode of treatment; the above numbers may therefore be accepted with confidence, as representing a close approximation to the average proportion of matter soluble in ether and alcohol contained in the normal products of guncotton manufactured according to von Lenk's prescription. In fifteen samples of guncotton prepared at Stowmarket in 1864, the lowest solubility was 2.85 per cent., the highest 12.55 per cent. The variations

exhibited by these numbers and the comparatively large proportion of soluble matter existing in some of the samples must unquestionably be ascribed to some irregularity in the treatment with acids as practised at Stowmarket, due perhaps to exceptional circumstances existing at the time these samples of guncotton were manufactured; the examination of several products of more recent date obtained from Stowmarket furnished much more uniform results, the majority of which correspond nearly to those obtained with the Waltham Abbey guncotton. Several of the specimens of guncotton obtained from Hirtenberg were also found to contain comparatively large quantities of soluble matter, and the proportions in two or three samples were very high. In nine samples the lowest solubility was 3.02 per cent. and the highest 14.21 per cent.

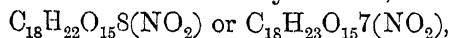
The character of the soluble matter extracted from the Waltham Abbey products by ether and alcohol was very uniform. The dry extracted matter, when digested with hot alcohol alone, dissolved to a very considerable extent, and a light yellow solution was obtained, which, on evaporation, furnished a yellow amorphous residue, almost entirely soluble in ammonia or sodium carbonate; the neutral liquids furnishing precipitates with lead and silver solutions. Ammonia was evolved when the substance was heated with potassium hydroxide. When gradually exposed to heat on platinum or bibulous paper, it first fused and then deflagrated. The portion insoluble in alcohol dissolved in the ethereal mixture, the solution furnishing on evaporation a semi-opaque film, which contracted and split up into small horny particles when quite dry. The extracts from Stowmarket and Hirtenberg guncotton contained the same product soluble in alcohol alone, and generally in about the same proportion; but in most of those instances in which the specimen had furnished a considerable proportion of soluble matter, the part insoluble in alcohol yielded by solution in ether and alcohol a liquid which approached in its character to photographic collodion, the film left by its evaporation being more or less tough and nearly transparent. In two instances very good photographs were obtained with the collodion extracted from specimens of Austrian guncotton. The percentage of matter soluble in alcohol alone was also determined, the lowest result being 0.72 per cent. and the highest result 0.95 per cent. The foregoing results show that, in general, in the

products of manufacture obtained by properly following von Lenk's instructions with regard to the conversion of cotton, the proportion extracted by alcohol alone is somewhat below 1 per cent., and consists of nitrogenized matter, of acid character, which has evidently been produced by the action of nitric acid upon the resinous or other foreign substances contained in the cotton at the time of its conversion. The portion soluble in ether and alcohol, but insoluble in spirit, varies in amount between 1 and 2 per cent., and consists of the very small proportion of guncotton which has escaped conversion into the most explosive product. The occurrence, in a few quite exceptional instances, of comparatively large proportions of soluble guncotton, of the kind produced by the action of a warm and somewhat dilute acid mixture upon cotton, affords important evidence of the necessity for adhering strictly to the mode of treatment and the precautions which considerable experience and a careful examination of products have proved to be indispensable for the attainment of uniform results in the manufacture of guncotton. With regard to the matter soluble in ether and alcohol found to exist in guncotton, the following observations possess some interest, as bearing upon the cause of its production in the manufacture of the substance.

1. The mean proportion of soluble matter furnished by the very concordant results of examination of guncotton manufactured at Waltham Abbey in 1863, in the preparation of which the acids, left in contact with the guncotton, were in the proportion of 18 parts by weight to 1 of cotton, is 1.62 per cent.; while the mean proportion furnished by the result of examination of sixteen samples of Waltham Abbey products, in the manufacture of which only 10 parts of the acid were left in contact with the guncotton, is 2.13 per cent. All the results obtained with the first guncotton were below 2 per cent., while out of sixteen results, obtained with the last, eleven were above 2 per cent. Here we have a decided indication that the prolonged contact with acid has some influence upon the composition of the product; the employment of the higher proportion of acid furnished results more nearly approaching perfection than those obtained when the guncotton was left in contact with a smaller proportion of the acid mixture. As far as can be judged at present, however, from the general properties of the products, the difference observed when the larger or the smaller propor-

tion of acid is used, is not of sufficient importance to render necessary the consumption of the larger quantity of acid in the manufacture.

2. The following experiment was instituted with a portion of one of the specimens of guncotton from Stowmarket, which had been found to contain 11·5 per cent. of matter soluble in ether and alcohol (after removal of the portion soluble in alcohol only). The guncotton, having been perfectly dried and carefully weighed, was digested for three hours with mixed nitric and sulphuric acids, of the kind always employed. It was afterwards submitted to long continued washings with distilled water; precautions being taken to prevent mechanical loss. The dry guncotton was found to have increased in weight 0·3 per cent. But the original guncotton contained 1·71 per cent. of mineral matter, while, after having been digested with acids and washed, it furnished only 1·01 per cent. of ash. The difference between these numbers had therefore to be added to the increase in weight which the guncotton sustained by this second treatment with acids, which consequently amounted to 1 per cent. The substance now no longer contained any appreciable amount of soluble matter. Assuming that the soluble guncotton originally existing in the sample was either one of those whose composition had been determined by Hadow,



the increase sustained by the imperfect sample, if completely converted into the most explosive and insoluble product, should have amounted in the one instance to 0·61 per cent. and in the other to 1·29 per cent. Considering that neither of these substances would be likely to exist alone in the imperfectly converted material, the actual increase of 1 per cent. sustained by the guncotton must be regarded as a close approximation to the theoretical proportion of imperfectly converted guncotton, and proves decisively that, on the one hand, the treatment of the cotton with the acids had not in the first instance been quite perfect, while, on the other, a further digestion of imperfectly converted guncotton with acids will convert soluble guncotton which it contains into the most explosive or insoluble variety.

Determination of the Carbon, Hydrogen and Nitrogen contained in Guncotton.—The difficulties which attend the application of the ordinary analytical methods to determining the composition of so highly explosive a substance as pyroxylin need scarcely

be dwelt upon. Several special methods of proceeding have been pointed out by different experimenters, and others have been elaborated in the course of these researches; but even the most simple and perfect require great care and some experience in their employment, for the attainment of trustworthy results. The following is a brief account of the most successful methods tried for determining the carbon, hydrogen, and nitrogen, and of the results which each has furnished. In the majority of instances the specimens of guncotton analyzed were ordinary products of manufacture. The material operated upon was always purified as far as possible from matter soluble in ether and alcohol, by repeated digestion and washing; and, in calculating the results, allowance was made for the mineral constituents of the guncotton operated upon.

Carbon Determinations: Method 1.—The guncotton yarn was cut into small pieces, dried, and the fragments introduced singly into a very long combustion tube, each portion being separated from the next by about 5 cm. of copper oxide. When the tube had received the entire quantity to be burned, about 15 cm. of the anterior portion were filled with copper oxide, and the remainder (about 20 cm.) with porous fragments of reduced copper. The potash apparatus, used for absorbing carbonic acid, had a small calcium chloride tube attached to it, which was weighed together with the apparatus, before and after the combustion. Although the greatest care was taken to proceed as slowly as possible with the heating of those portions of the tube containing the guncotton, the successful completion of the operation was a matter of great uncertainty, as the explosive combustion of some small portion of the guncotton would very frequently throw the surrounding copper oxide forward, thus closing the necessary passage in the front part of the tube. This method was therefore abandoned after about two dozen experiments had been made, of which only four were brought to a satisfactory termination. The mean result of the four samples was 24.02 per cent. of carbon.

Method 2.—The weighed substance was saturated with distilled water, and the latter removed as far as possible by pressure. The moist yarn was then cut into eight or ten pieces and introduced separately into one end of a long combustion tube open at both extremities, and divided in the centre by a plug of asbestos. The shorter portion of the tube contained

only the fragments of guncotton placed at a distance of about 12 mm. from each other; the longer portion was previously filled with long layers of copper oxide, oxidized copper turnings and porous reduced copper. This part of the tube was connected with a desiccating apparatus, to which were attached the potash bulbs with the small weighed calcium chloride tube fixed on to the outer limb. The extremity of that part of the combustion tube which contained the guncotton was connected with an arrangement for passing an easily regulated current of pure dry air through the apparatus. The two portions of the tube were separated in the furnace by a screen. When the front part of the tube had been raised to a full red heat (at which it was maintained throughout the operation), the pieces of guncotton were consecutively made to undergo slow combustion, the portion nearest the asbestos plug being first heated, and the resulting gases and aqueous vapours being carried forward by the slow current of air continuously passed through the apparatus. This passage of air served to oxidize minute portions of carbon separated from the guncotton, when the whole tube was raised to a red heat at the close of the operation. The proportion of the reduced copper employed was so regulated, that a considerable quantity remained unoxidized at the conclusion of the experiment. Great care was required in the application of heat to the parts of the tube containing the moist guncotton, there being otherwise considerable risk of its fracture by the water expelled from the heated substance. The quantities of material operated upon ranged from 0.2634 gm. to 0.4115 gm. The mean of four determinations on different samples of guncotton manufactured in 1863 was 24.42 per cent. of carbon.

Method 3.—A weighed quantity of guncotton, moistened as in the preceding experiments, was placed in a capacious strong Bohemian glass tube, sealed at one end; a small quantity of copper oxide was introduced into the tube just in front of the guncotton. The other extremity of the tube was now constricted, and was sealed when the air in the tube had been exhausted. Heat was then carefully applied to the sealed tube until the guncotton had undergone slow combustion, and the oxide of copper was afterwards shaken to that part of the tube where a minute carbonaceous deposit had been left by the guncotton. The tube was placed in a gas furnace and connected at one end with an apparatus for delivering pure air and oxygen,

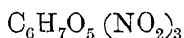
and at the other with a long combustion tube, in a separate furnace, containing layers of oxide of copper and porous reduced copper, to which were attached a large calcium chloride tube and the potash apparatus. The two Bohemian tubes were connected by a narrow indiarubber tube, about 12 cm. long, fitted with a screw clamp, so that communication between the tubes could be cut off or gradually increased. The long tube having been raised to a red heat, the point of the sealed tube which was enclosed in the rubber connection was broken, and the confined gases were allowed to pass gradually over the heated copper oxide and metal. When no further escape of gas from the tube took place, the other extremity, connected with the apparatus for delivering air, was broken, and the whole of the products of decomposition of the guncotton were gradually conveyed into the heated tube. Pure oxygen was finally passed through the apparatus, and the tube, in which the guncotton had been burned, was heated to redness. The guncotton for these experiments was taken from various products of Waltham Abbey manufacture obtained in 1863 and 1864; the quantity employed varied between 0.2257 grm. and 0.39 grm. The mean of four determinations was 24.15 per cent. of carbon.

Method 4.—The guncotton was reduced, by cutting, to an extremely fine state of division, and mixed when dry as intimately as possible with a very large proportion of lead chromate in the first few experiments, and of finely divided copper oxide in the remainder. Long layers of copper oxide and porous reduced copper were employed as usual, and at the close of the combustion a current of pure oxygen, and finally pure air, was passed through the tube. With care and experience, the combustion of the substance was brought perfectly under control by this comparatively simple method of proceeding; in a few instances, however, the operation was terminated prematurely by the stopping up of the tube, in consequence of the explosive combustion of a small accumulation of the finely divided guncotton. The mean of 14 determinations was 24.57 per cent. of carbon. This gives as a mean of 49 determinations 24.29 per cent. of carbon. The results, however, upon the accuracy of which the most perfect reliance is to be placed, are unquestionably those furnished by the fourth method, which ranged between 24.04 per cent. and 24.88 per cent., the mean being 24.57 per cent.

Determination of Hydrogen.—The hydrogen was determined at the same time as the carbon, by the method of operating last described. The results of all the combustions (eight in number), conducted with different samples of guncotton yarn, were so remarkably uniform, that they were regarded as furnishing ample numerical data with respect to this element. The mean of four determinations was 2.46 per cent. of hydrogen.

Determination of Nitrogen.—The method of Dumas was employed for determining, by volume, the proportion of nitrogen contained in guncotton. A rather wide combustion tube, about 82 cm. long, was drawn out at one end so as to admit of being connected with a carbonic acid apparatus provided with a regulating tap, and was fitted at the other end with the usual form of delivery tube. 5 cm. of the tube were first filled with coarse porous fragments of copper oxide, a layer of 3 cm. of fine copper oxide followed, and then the very finely cut guncotton, mixed with a large proportion of copper oxide; the mixture occupying about 25 cm. of the tube. The next 22 cm. were filled partly with coarse porous copper oxide, and partly with finely powdered oxide; a layer of 20 cm. of reduced copper followed; and finally, the tube was plugged with coarse porous oxide, occupying a length of about 5 cm. The combustion was conducted very slowly, with the usual precautions, pure carbonic acid being passed through the apparatus for the requisite period before commencing, and at the conclusion. The gas collected was found, in one instance only, to contain traces of nitric oxide, and this determination was consequently rejected. The quantity of substance operated upon varied between 0.3006 gm. and 0.415 gm. The results of 18 analyses of various products from Waltham Abbey ranged between 13.36 per cent. and 14.60 per cent., with a mean of 13.83 per cent. of nitrogen.

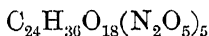
Deductions from the Analytical Results.—The formula adopted by Hadow, as representing the most explosive product of the action of mixed nitric and sulphuric acids upon cellulose, which is the same as that first suggested for guncotton by W. Crum, afterwards adopted as probable by Gerhardt, and recently supported by Schrotter, Redtenbacher and Schneider, demands the following formula:—



which represents the following composition:—

C., 24.24%; H., 2.36%; N., 14.14%; O., 59.26%.

The formula adopted by Pelouze and Maury, as agreeing closely with the results which they obtained in their experiments, was as follows:—



representing the following composition:—

C., 25.00%; H., 3.13%; N., 12.15%; O., 59.72%.

The results obtained from Waltham Abbey guncotton show it to approximate quite closely to that required for the formula for trinitrocellulose.

In comparing the experimental results with the requirements of the two different formulæ, it is necessary to bear in mind the following circumstances:—

1. The guncotton examined has not been obtained from pure cellulose (for the production of which the most elaborate system of purification has been proved necessary), but has been prepared from cotton separated from foreign matter, as far as it is possible, by the ordinary method of purification adopted.

2. Ample proof has been furnished, by most extensive and rigorous experiments, of the invariable existence in the purified guncotton (as produced by the most complete action of the strongest acids upon cotton-wool, purified by treatment with alkali and washing) of notable proportions of substances which owe their existence to the presence of foreign matter remaining in the cotton fibre after its ordinary purification, and also of products resulting from the less perfect action of nitric acid upon small portions of the cellulose.

3. Although these two varieties of impurities were extracted, as far as possible, by repeated digestion and washing with ether and alcohol, their perfect removal from the fibre, by the application of any feasible method of purification, is extremely difficult, if not impossible.

4. The existence of even small proportions of these impurities in a sample of pyroxylin will have the effect of raising somewhat the percentage of carbon obtained by analysis of the substance above that which would be furnished by the pure material, and also, consequently, of reducing, to a trifling extent, the proportion of nitrogen obtained below the theoretical requirement. A proof of this is furnished by the analytical results obtained with specimens of the matter soluble in ether and alcohol, which had been extracted from Waltham Abbey guncotton.

The results were as follows:—

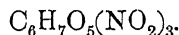
For the soluble portion—

C., 30·50%; H., 2·91%; N., 11·85%.

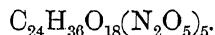
For the portion insoluble in ether-alcohol—

C., 24·15%; H., 2·46%; N., 13·83%.

It is believed that the foregoing circumstances must be admitted to account perfectly for the slight variations exhibited, among themselves, by the numerous analytical results which have been quoted. The whole of the carbon percentages obtained by the most trustworthy method of analysis (Method 4) are somewhat higher, and the great majority of the results of the nitrogen determinations are a little lower than required by the formula



On the other hand, making every full allowance for errors of analysis, and assuming for an instant the possibility that the substance analyzed could be an absolutely pure product, the individual as well as the mean results of the carbon, hydrogen and nitrogen determinations, are far more closely in accordance with those theoretical requirements, than with the percentage results which should be furnished by a pure substance, having the composition more recently assigned to pyroxylin by Pelouze and Maury, viz.—



The analytical results of guncotton manufactured at Waltham Abbey according to von Lenk's directions confirm, therefore, the correctness of the conclusions that the most explosive known variety of guncotton is trinitrocellulose or trinitric-cellulose; and that cotton wool is converted into this substance by the complete action upon it, in the cold, of a mixture of one part by weight of nitric acid (1·52) and three parts of sulphuric acid (1·84). In addition to the data furnished by the analytical experiments described in the foregoing, others, bearing upon the composition of guncotton, have been furnished by different systems of experimental inquiry.

The relation between the nitrogen and carbonic acid obtained by oxidation of guncotton has been determined. For this purpose, Liebig's method of operating was adopted in the first instance; the guncotton being prepared and arranged for combustion as in the case of the nitrogen determinations, and the mixed gases collected in successive proportions and examined. A few experiments rendered it evident, however, that this

method, when applied to the examination of guncotton, did not furnish trustworthy results. In the decomposition of this substance, when distributed through a very large proportion of copper oxide, the oxidation of the carbon does not proceed uniformly; small portions of that element evidently escape oxidation in the first instance, and are only subsequently burned when the nitrogen has already been in great proportion liberated. The proportion which the carbonic acid bears to the nitrogen in the gases successively collected varies, therefore, frequently, as the combustion proceeds; and it would consequently be necessary to collect the entire quantity of gases furnished by the guncotton operated upon, in order to arrive at a correct result. The following statement of the relative proportions by volume of the gases collected successively in two operations of this kind will serve to illustrate the variable composition of the gas collected at successive stages of one and the same operation. In both experiments the gas had been allowed to escape for some time before the first collection, for expulsion of the air in the combustion tube. The results varied from 77.45 per cent. of carbonic acid and 22.55 per cent. of nitrogen to 80 per cent. of carbonic acid and 20 per cent. of nitrogen. The majority of results obtained in each of the above experiments are concordant among themselves, and agree closely with the percentage proportions (by volume) of carbonic acid and nitrogen which should be furnished by trinitrocellulose (namely, 80 of carbonic acid to 20 of nitrogen). But in each experiment somewhat discordant results were obtained, and therefore this method of determining the relation between the carbon and nitrogen in guncotton was abandoned as not sufficiently trustworthy. It should be observed, however, that even the mean of the several results obtained in each experiment corresponds much more closely with the volume-proportion which should be furnished by trinitrocellulose than with that demanded by the formula which Pelouze and Maury adopted.

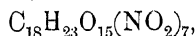
Several determinations of the relative proportions of carbonic acid and nitrogen have been made by Bunsen's method. The mode of operating was as follows. Into a very stout wide Bohemian glass tube, about 22 cm. long and sealed at one end, were introduced, first some reduced copper, then about 0.1 to 0.15 grm. of the dry guncotton, and afterwards sufficient oxide to fill about 4 cm. of the tube. The open extremity of the latter

was constricted, and sealed when the air had been exhausted. The guncotton was then decomposed by applying the flame of a lamp to the tube for a short time. After the oxide of copper had been distributed over the surface of the tube (to the interior of which it adhered, in consequence of the deposition of water from the exploded guncotton upon the glass), the latter was introduced into a vessel of wrought iron, within which it was compactly surrounded on all sides by very fine sand. The vessel consisted simply of a piece of gas-pipe about 25 cm. long and of 3 cm. internal diameter, closed at one end by means of a plug welded into it, and provided at the other extremity with a screw-cap. A few small perforations were drilled into the sides of the pipe. The glass tube was exposed in this envelope to a red heat for about an hour; when cold, it was opened under mercury, and the gas transferred and examined in the usual manner. The results thus arrived at, which will be quoted presently, were very concordant, and stood in close relation to the results obtained by the separate determinations of carbon and nitrogen in guncotton.

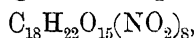
The reproduction of cotton from guncotton by Hadow's method has been made the subject of many experiments, with the view of controlling by its means the analytical and synthetical results obtained. It was found that by submitting purified insoluble guncotton to the action of an alcoholic solution of potassium hydrogen sulphide, as directed by Hadow, the amount of cotton obtained corresponded closely to the theoretical proportion which should be furnished by trinitrocellulose. The following results may be quoted as examples. They were obtained with guncotton which contained only small proportions of matter soluble in ether and alcohol. From 4.064 to 4.898 grms. of substance were employed. The theoretical percentage of cotton produced from trinitrocellulose is 54.54 per cent. From 9 different samples of guncotton the results varied from 53.64 percent. to 55.38 percent. In conducting experiments by this method of examination, a liability to mechanical loss was observed when a very strong solution of the potassium hydrogen sulphide was employed, in consequence of the fibre becoming, to a considerable extent, disintegrated during the digestion; but this can be easily avoided by employing the reagent in a more dilute form. The solution best adapted for effecting the complete reduction of guncotton by digestion in the cold without

breaking up the fibre was obtained by preparing a saturated solution of potassium hydroxide, completely saturating this with hydrogen sulphide, and diluting the liquid thus obtained with half its volume of alcohol. A small loss of product generally occurs, even when the sulphide solution is not stronger than just described, in consequence of a feeble solvent action exerted by the liquid upon the reduced cotton. In one experiment a sample of cotton obtained from guncotton sustained a loss of 0.6 per cent. by digestion in the cold for forty-eight hours with the sulphide solution. A slight excess (about 0.5 per cent.) is sometimes exhibited by the weight of the reduced cotton over the amount which should be furnished, theoretically, by pure trinitro-cellulose. In order to ascertain how far this might be ascribed to the retention of sulphur by the cotton under treatment, a very careful examination of several specimens was instituted. A faint odour of sulphurous acid was sometimes observed when the reduced cotton was burned, and in two or three instances the cotton sustained a slight loss (from 0.1 to 0.3 per cent.) upon being digested and washed with carbon disulphide; but in other instances the proportion present was only very minute, and the cotton was generally found to be quite free from sulphur. A comparison between the ash existing in the guncotton showed that no proportion of an excessive result can be ascribed to an accumulation of that constituent. Although the amount of guncotton operated upon is about double that of the cotton recovered, the latter was found to contain the smallest proportion of ash. It is evident that the mineral impurities which, during the washing operations, have attached themselves to the guncotton fibre, become partially detached during the digestion in sulphide solution and the subsequent washing. Some combustions made of the reduced cotton furnished proportions of carbon and hydrogen which, though according fairly with the requirements of pure cellulose (allowance being made for the ash in the specimens analyzed), were somewhat below the theoretical numbers. The theoretical percentage of carbon in cellulose is 44.44 per cent. The amount found was 43.98 per cent. The specimens analyzed were carefully examined for nitrogen, and very small quantities were detected. The deficiencies of the carbon obtained from them may, therefore, be to a slight extent ascribable to minute portions of the nitro-product having escaped reduction. A still greater influence upon the results

must, however, be exerted by the invariable existence of small quantities of foreign organic substances in the samples operated upon. The slight excess obtained, in many instances, above the theoretical amount of cotton may, it appears, be occasionally due to some extent to accidental causes, but it is mainly to be ascribed to the presence in the specimen examined of a proportion of material resulting from the less perfect action of nitric acid upon some portions of the cotton fibre. Unfortunately, however, the fluctuations in the results which may be furnished by different examinations of the same specimen of guncotton by this method, though they might be regarded as not very important in an ordinary analytical process, may be equivalent to differences which would be caused by very considerable variation in the amount of soluble guncotton present in the substance. Supposing that the matter soluble in ether and alcohol in a specimen of guncotton amounted to 2 per cent. and consisted of the compound



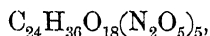
the result of the analysis should be affected by that impurity to the extent of about 0.1 per cent. An excess of 0.5 per cent. obtained in the examination of a sample should therefore indicate the existence of 10 per cent. of the above compound (readily soluble guncotton) in the sample; or if the specimen contained that percentage of a compound



this would only affect the result by 0.3 per cent. It cannot be confidently asserted that the errors of the method itself are ever less than from 0.3 per cent. to 0.5 per cent. It is evident, therefore, that this method of examining guncotton, though useful as a mode of controlling the results obtained by determining the increase of weight which cotton sustains by treatment with nitric acid under varied circumstances, is not susceptible of affording sufficiently definite and trustworthy results to render it applicable as a method of ascertaining the degree of freedom from soluble guncotton of products of manufacture.

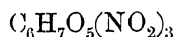
Experiments on the Increase sustained by Cotton in its Conversion into Guncotton.—Hadow found that cotton-wool, by treatment with the strongest mixture of nitric and sulphuric acids, sustained an increase of 81.34 per cent., that the guncotton produced was quite insoluble in mixtures of ether and

alcohol, and that the increase of weight which cellulose should sustain by conversion into the trinitrocellulose agreed very nearly with the results of his experiment. Pelouze's earlier experiments fixed the maximum increase in weight sustained by cotton upon conversion into guncotton at 76 per cent. But in the recent report of Pelouze and Maury it is stated that, in a number of laboratory experiments in which the composition of the acid mixture, the proportions borne by the acid used to the cotton treated, and the duration of the treatment, were variously modified, the increase in the weight of the cotton fluctuated within narrow limits, and did not exceed 78 per cent. The authors are led, mainly by these results, to adopt the formula



because cellulose, by conversion into a substance having the percentage composition which that formula demands, should sustain an increase of weight of 77·78; a number which is very slightly *below* the maximum results obtained in their experiments. It should be stated that they describe the acids employed by them in all their experiments as follows: The sulphuric acid had a density of 66° Baumé (which corresponds to a sp. gr. of 1·767), and the nitric acid had a specific gravity of 1·50 at 9° C. It will be observed that these acids, but more especially the sulphuric acid, are very notably inferior in strength to those prescribed by von Lenk, which have been used in all the experiments now described, and are always employed in the manufacture of guncotton at Waltham Abbey; namely, sulphuric acid of sp. gr. 1·833 to 1·84 (somewhat above 69° Baumé), and nitric acid of sp. gr. 1·52 at 15° C. It appears most probable, from many of the experimental observations included in these researches, that such discrepancies as exist between the results arrived at by Pelouze and Maury, and by Hadow, the German chemists and myself, are to be mainly ascribed to the differences in the strength of the acids employed. The subjoined results of very numerous experiments will, I believe, be admitted not only to establish satisfactorily the correctness of Hadow's statement, that cotton-wool may be made to sustain an increase in weight above 81 per cent., but also to show that the results of other experimenters who have found the increase sustained by cotton not to exceed 78 per cent., are in perfect harmony with the conclusion that the product of the complete action, upon

cotton-wool, of certain mixtures of the strongest nitric and sulphuric acids, is the substance

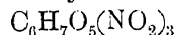


in a nearly pure condition. Experiments where guncotton was subjected to repeated immersion in fresh mixtures of acids, where the proportion of acid to cotton was about 60 to 1, showed that 100 parts of cotton increased in weight to 182.13, a number somewhat higher than that obtained by Hadow. By protracting the treatment beyond the point when the product ceased to increase in weight, a slight but continuous loss was sustained, which, there appears no doubt, from the results of confirmatory experiments, is to be ascribed to the solution of small quantities of guncotton in the strong acids with which it was left in prolonged contact. Repeated immersion of cotton in an acid mixture of somewhat less strength does not effect, nearly as rapidly or as completely, its conversion into insoluble guncotton, as does a single treatment with the acid mixture prescribed by von Lenk. Experiments in which the proportion of acid to cotton was 50 to 1 showed that by a single treatment of cotton with a considerable proportion of the strongest acid mixture, results may be obtained closely in accordance with the number given by Hadow, and with the theoretical requirement of trinitrocellulose. The mean of these experiments fixes the maximum increase in weight which cotton is capable of attaining by this treatment at 82.16 per cent.; the theoretical number is 83.3 per cent. Where the proportion of acid to cotton was 10 to 1, and the time of contact 12 to 48 hours, the conversion into trinitrocellulose cannot be completely accomplished. In these instances the increase of weight sustained by the cotton is between 78 and 80 per cent. As might have been anticipated, the products contained notable proportions of matter soluble in ether and alcohol, while those obtained in the experiments with a larger proportion of acids yielded only a minute trace to the action of the solvent.

Where the proportion of acid to cotton was 50 to 1, and the time of immersion only ten minutes, the importance of continuing the digestion with acids longer than is merely necessary for the production of an explosive material was clearly shown. By immersion for ten minutes only the cotton increased in weight 62.43 per cent., and the product was to a considerable

extent soluble in ether and alcohol. In another experiment a still more soluble product was obtained by immersion for only three minutes. Where the quantity of acid is limited, digestion for 12 hours is scarcely sufficient to ensure the maximum attainable increase of weight; under equal conditions the results obtained by immersion for 24 hours were quite equal to those furnished by more protracted digestion. This observation was fully borne out by the results of manufacturing operations. There was no doubt that an actual loss of product, though only slight, was sustained by prolonging the contact of the acids with the guncotton much beyond the period necessary for its perfect production. It was shown that a very brief treatment of cotton with a warm acid mixture effects its conversion into soluble guncotton as completely as a long-continued treatment with cold acids (the proportion of the latter being limited). This experiment was made for the purpose of ascertaining whether, with the employment of the strongest acids, heat exerted a similar influence upon the character of the product to what it does when weaker acid mixtures or mixtures of saltpetre and sulphuric acid are employed. This is evidently not the case, for the product obtained was as slightly soluble as the general products of manufacture at Waltham Abbey. It was also found that a few minutes' immersion in a warm acid mixture converted an imperfect product, obtained with a few minutes' treatment with *cold* acids and containing much soluble matter, into a guncotton of the ordinary kind. The results furnished, under most favourable circumstances, by cotton of an ordinary commercial quality varied between 78 and 81 per cent., never quite reaching the latter number. The results also point, as did some of those obtained with the purer cotton, to a tendency of the guncotton to dissolve in the acid mixture when the immersion is continued for a very long period. Results obtained by treatment of the cotton for 24 hours were notably higher than those furnished by the 48 hours' treatment. The loss of product ascribable to this cause was doubtless somewhat greater in these experiments than in manufacturing operations, when the proportion of acid to the cotton is considerably lower. A comparison of the weight of cotton, obtained from samples of guncotton, with the original weight of cotton employed in their production, affords data which are strongly in support of the conclusion that the differences between the increase in weight

which cotton should sustain by conversion into trinitrocellulose



and the results furnished by as perfect a treatment of different specimens of cotton as is practicable, are to be ascribed, not merely to the presence, in the products, of small quantities of imperfectly converted soluble guncotton, but also to the existence in them of substances which are foreign to the cotton, and which are only partially removable by simple washing with water. Using Hadow's method for the regeneration of cotton from nitrocellulose, it was shown that cotton which was recovered from the laboratory products, furnished by comparatively very pure cotton which had sustained an increase of weight of 82 and 82.6 per cent. (the theoretical increase being 83.3 per cent.), amounted to only about 1 per cent. less than the cotton originally taken; and that when the employment of a limited quantity of acid yielded a product the weight of which represented about 2 per cent. less increase than these, the cotton recovered was in this instance only about 1 per cent. below the quantity employed, the difference in the weight of the nitro-product having been due only to the formation of a somewhat larger proportion of soluble guncotton. It appears from these results, and estimating the proportion of loss which the processes of conversion and reduction may involve at about 0.5 per cent., that the particular cotton-wool operated upon contained about 0.5 per cent. of matter foreign to cellulose, which was eliminated in the course of the transformation and reproduction of the latter. But, when less pure samples of cotton were converted, as completely as practicable, into insoluble guncotton, and furnished results from 1.74 to 4 per cent. lower than those obtained by a similar treatment of the pure material, the weight of the recovered cotton indicated a loss, upon the original substance employed, of from 4.4 to 6.3 per cent.; an increased loss which must be due to the larger proportion of foreign matters existing in the cotton operated upon. These facts surely afford strong support to the conclusion that the deficiency in weight exhibited by the products obtained from ordinary cotton-wool, even after its purification with alkali, as compared with those furnished under the same circumstances by purer cotton-wool, is due to the presence of foreign matters in the cotton, which though partially retained by the guncotton, exist there in the form of products whose formation does not add, in so high a

proportion, to the original weight of the cotton as does the production of trinitrocellulose.

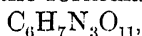
Two quantitative operations were conducted in the ordinary course of manufacture at Waltham Abbey, with the view of ascertaining the actual quantity of guncotton furnished by 100 parts of cotton in the ordinary course of operating with considerable quantities of material. In one experiment the cotton employed, which contained about the average quantity of seed, and had, as usual, the peculiar colour of unbleached fibre, was submitted to the ordinary purification in the bath of potassium carbonate, and was dried as usual for twenty-four hours at 50° C. before immersion in acids. Its weight, when dry, was 31 lbs. 6 ozs. It was afterwards treated in all respects like an ordinary product of manufacture. The weight of the air-dry guncotton showed an increase upon the original dry cotton of 74.3 upon 100 parts. The weight of the thoroughly dry product corresponded to an increase of 71 upon 100. In another experiment, made with a somewhat higher quality of cotton, an increase of 76 per cent. was obtained. The products of these operations were quite similar in character to those usually obtained, and to the results furnished by the laboratory experiments previously described, which were conducted with samples of the same description of cotton. A difference of about 9 per cent. between the latter results and the lowest number furnished by the quantitative manufacturing experiments had therefore to be accounted for. The following statements show that this deficiency was not greater than would be anticipated. In the cotton operated upon, besides the resinous and other impurities which are partly removed by solution in the acid, and by subsequent extraction in the purifying processes, and which also occasion a notable loss in the laboratory experiments with this kind of cotton, as already pointed out, there exists a more or less considerable proportion of seed, of which only minute particles are here and there observed in the finished guncotton. To this source of loss upon the weight of the cotton employed has to be added the mechanical loss of product unavoidably attending the repeated submission of the guncotton to the expressing and long-continued washing process. But the principal loss of product, and one which alone suffices to account for the difference observed between the results of the laboratory experiments and those of ordinary manufacturing operations,

occurs in boiling the guncotton in the alkaline bath. The brief digestion of the material in the weak solution of potassium carbonate not only abstracts a considerable proportion of the products foreign to guncotton, resulting from the action of the acids upon the impurities which the cotton fibre obstinately retains, but also causes a very notable proportion of the guncotton itself to pass into solution. A quantity of Waltham Abbey guncotton which had, in the ordinary course, already been submitted to the treatment with alkali, was boiled for ten minutes in a solution of potassium carbonate precisely similar to that usually employed (sp. gr. 1.02). The liquid became of an amber colour, and the guncotton, when dried, was found to have sustained a loss of 3.7 per cent. The same guncotton was again boiled for twenty minutes in the same alkaline bath, which deepened in colour considerably during this second employment. The total loss sustained by the material after this second treatment amounted to 12.09 per cent.

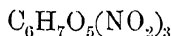
Nine grms. of cotton yarn, previously purified by treatment with alkali and carefully freed from seed, were converted into guncotton in the ordinary manner, excepting that about three times the ordinary proportion of acid was used, whereby the solution of foreign matters in the acid was promoted. The product, after long continued washing in distilled water, was dried and weighed. The increase sustained by the cotton amounted to 78.14 per cent. (a number closely corresponding to the laboratory results previously described). The guncotton was then boiled for eleven minutes in a solution of potassium carbonate of the usual strength. When washed and again dried, it was found to have lost considerably in weight, and the finished product showed an increase of weight upon the original cotton equivalent to 69.8 upon 100, which was therefore 1.2 per cent. less than the lowest result obtained in the manufacturing operations. It is easily conceivable that, in the smaller operations, the guncotton, though submitted for only exactly the usual period to treatment with an alkaline bath of the ordinary strength, should sustain a somewhat greater loss than a large compact mass of the material, such as is always operated upon. But the results of these experiments establish a source of loss in the usual process of manufacture, which fully accounts for the discrepancies exhibited between the yields of usual manufacturing operations and of laboratory operations conducted with the same descrip-

tion of cotton, in which the treatment with boiling alkaline water has been omitted.

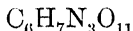
Comparison between Analytical and Synthetical Results.—The relative proportions of carbonic acid and nitrogen furnished by the complete oxidation of guncotton, afford the means of instituting a comparison between the analytical and synthetical results of which the details have been given, and, it is believed, of demonstrating beyond dispute the correctness of the conclusion, that the product of the complete action upon cotton-wool of the mixture of strongest acids prescribed by von Lenk is most correctly represented by the formula



of which the expression



appears to be the most rational interpretation. From the relative volumes of carbonic acid and nitrogen furnished from the guncotton, it appeared that the nitrogen, though somewhat low, is nearer to the requirements of the trinitrocellulose formula than to those of the formula adopted by Pelouze and Maury; the proportions of the gases observed in three experiments, which happened to be identical in their results, corresponded with the requirements of



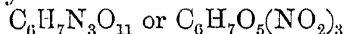
as closely as could possibly be expected when operating upon a substance of approximate purity only. Upon calculating the proportion which the nitrogen found (13.32 and 13.59 per cent.) in these experiments bears to the mean percentage of carbon (24.6) obtained by the most trustworthy method employed for the determination of that element, it was evident that these percentage proportions of nitrogen were not only in perfect accordance with a considerable number of results obtained by direct determination of the volume of nitrogen furnished by samples of Waltham Abbey guncotton; but they were also as close approximations to the theoretical percentage of nitrogen in trinitrocellulose as the analysis of products containing small proportions of lower nitro-compounds could be expected to furnish; and lastly, the increase in weight which cotton of average purity should sustain by conversion into nitrocellulose products which furnish these proportions of nitrogen, corresponded closely to the average results obtained by operating upon moderately pure cotton with the mixed acids of *prescribed*

strength and in the proportion (about 10 parts to 1 of cotton) indicated by von Lenk.

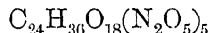
Abel's general conclusions were as follows:—

1. The products obtained by submitting cotton-wool to treatment with the prescribed mixture of nitric and sulphuric acids, and to purification as directed by von Lenk, are very uniform in character; they consist almost entirely of the most explosive known variety of guncotton or pyroxylin, which is insoluble in mixtures of ether and alcohol. This substance, when produced upon a manufacturing scale, contains from 1 to 2 per cent. of mineral substances, and a small proportion, varying with the quality of the cotton, of matters soluble in alcohol, partaking of acid properties, and consisting chiefly, if not entirely, of products of the action of nitric acid upon resinous or other bodies enclosed in the cotton fibre. There is also always present in the guncotton a small quantity (from 1 to 3 per cent.) of cellulose-products of a less explosive character, soluble in mixtures of ether and alcohol, which result from the incomplete action of nitric acid upon small portions of the cotton operated upon.

2. The guncotton, when purified, as far as it is possible, from foreign substances, soluble in alcohol and in ether and alcohol, furnishes analytical results which agree much more closely with those demanded by the formula



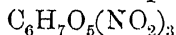
than with the requirements of the formula



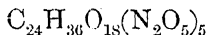
recently adopted for guncotton by Pelouze and Maury.

3. If cotton-wool of great purity is digested for a period of about twenty-four hours with a considerable proportion of the prescribed acid mixture (about 50 parts to 1 of cotton) it sustains an increase of weight ranging between 81.8 and 82.6 upon 100 of cotton. Lower results (between 78 and 80 per cent. increase) are obtained by digesting the cotton for a short period only, or for very considerable periods, by using a limited proportion of the acid (from 10 to 14 parts to 1 of cotton), by employment of acids of slightly lower specific gravities than those specified, and by operating upon cotton of somewhat lower quality. The digestion, for a second or third time, of products which have exhibited a comparatively low increase of weight, in an acid-mixture of the kind first used, or of greater strength, has the

effect of raising the weight of the product to within the higher limits above named. The increase in weight which 100 parts of pure cellulose should sustain, theoretically, by complete conversion into a substance of the composition



is 83.3, while if converted into a substance of the formula



the increase sustained by it only amounts to 77.8 upon 100 parts.

4. Cotton-wool always contains, even after careful purification, small proportions of foreign organic substances, the presence of which, in the material submitted to treatment with the acids, must affect to some extent the quantity of the product obtained.

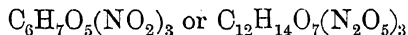
5. It is extremely difficult, indeed apparently impossible, even in operating under most favourable conditions upon small quantities of cotton-wool, to convert this substance *completely* into the highest nitric product—the perfectly insoluble guncotton. Small quantities of guncotton soluble in ether and alcohol can always be extracted from the products; the quantities are only minute in the highest laboratory products, but they are always very appreciable in the most perfect manufacturing products. Their invariable formation must unquestionably cause the increase of weight sustained by cotton to be somewhat less than that which theory would demand.

6. The long-continued digestion of the guncotton in the acid mixture, the several mechanical operations to which it is submitted in the course of its purification, and above all, the solvent action exerted not only upon certain by-products, but also upon the guncotton itself by the alkaline liquid, in which it is boiled for a short time, are all sources of loss which, in examining into the results of a system of manufacture, must not be disregarded, and the existence of which explains satisfactorily the difference observed between the weights of the laboratory products and those of manufacturing operations.

7. In accepting the formula proposed by Pelouze and Maury for guncotton, it would be necessary to assume that the cotton-wool operated upon was pure cellulose; that the operation of conversion was an absolutely perfect chemical process; that there were no possible sources of loss in the production of the material; and that in all laboratory operations which had furnished an increase of weight above the theoretical demand (77.8 per cent.), some substance differing in composition from

the ordinary products of manufacture must have been obtained.

8. The identity in their characters, and close resemblance in composition, of the most perfect products of laboratory operations and of the *purified* products of manufacture, the very close approximation in the weight of the former to the theoretical demands of the formula



and the satisfactory manner in which the unavoidable production of somewhat lower results in the manufacturing operations admits of practical demonstration, appear to afford conclusive evidence of the correctness of either of those formulæ as representing the composition of the most explosive guncotton, and to demonstrate satisfactorily that the material, prepared by von Lenk, consists uniformly of that substance (now generally known as *trinitrocellulose*) in a nearly pure condition.

CHAPTER XIII

ABEL ON THE STABILITY OF GUNCOTTON (1867)¹

THE earlier of the published researches into the composition and properties of guncotton were speedily followed by accounts of the spontaneous decomposition which the substance was, in many instances, observed to undergo upon more or less protracted exposure in confined spaces to strong or diffused light. These indications of instability, in conjunction with the occurrence of several serious explosions during the manufacture of guncotton in France and England, afforded apparently good grounds for the general conclusion—arrived at within a brief period after the announcement of Schönbein's discovery, and adhered to until quite recently in all countries except Austria—that this remarkable explosive agent did not in itself possess the quality of uniform permanence essential to its safe manufacture, or to its employment with any degree of security from accident, in warlike or industrial operations. It is unnecessary to refer in detail to the results of the numerous observations published before 1860 upon the nature of the spontaneous changes which particular specimens of guncotton had suffered. In the brief prefatory review of published investigations upon the production and composition of guncotton, contained in the paper on those subjects which was communicated to the Royal Society in 1866, it was shown that the products obtained by individual operators in submitting cotton to the action of nitric acid varied greatly in composition, and that, with only one or two exceptions, these could not be viewed as representing the definite substance producible by the most complete action, at a low temperature of a mixture of the strongest nitric and sulphuric acids upon purified cotton wool (or nearly pure cellulose). The behaviour and results of the decomposition of such specimens, or of others of more recent date prepared (for lectures or similar experimental purposes), without special regard being paid to their composition or purity, afford but little information that can be

¹ *Trans. Roy. Soc.* (1867), 181-253.

accepted as bearing upon the question of the stability of guncotton when produced by a system of operation which is now known to furnish uniform products in a condition of comparative purity. There can be no question that the variations in composition of the different specimens of guncotton, the decomposition of which has received investigation at different hands, exerted a most important influence upon the period for which they withstood the destructive effects of heat and light, and upon the *degree of rapidity* with which chemical change, when once established, proceeded from stage to stage. The *products* of change described by different observers have also varied somewhat in their characters, partly on account of the variations in the guncotton itself, and partly because different experimenters have examined the products of its metamorphosis at different stages. The accounts published by De Luca, Bonet and Blondeau, between 1861 and 1865, of their investigations into the changes which guncotton undergoes spontaneously, include nearly all the results previously described in one or other of the published papers on this subject.

The following is a general statement of the changes which guncotton, preserved in bottles partly, or perfectly closed, has been observed to undergo by exposure to light, and of the nature of the products of decomposition. In the first instance nitrous vapours make their appearance, the atmosphere in the vessel becoming sometimes of a deep orange tint. The guncotton acquires considerable acidity, exhibits a peculiar pungent odour, and generally contracts, so that it eventually occupies only a small proportion of the original volume. During this period a considerable proportion of nitric acid accumulates in the mass, and the decomposition proceeds after a time with increased rapidity, especially if the vessel be exposed to sunlight. The contracted guncotton gradually becomes more or less friable, its explosiveness is notably reduced, it yields a highly acid extract to water, in which, besides nitric acid, small proportions of glucose, of formic and oxalic acids, and of cyanogen have been detected. The material sometimes contracts to such an extent as to form a very compact and somewhat hard mass, but in general it ultimately passes over with more or less rapidity into a brownish gum-like mass, which at first is rendered very porous by the evolution of gas bubbles, and which becomes lighter in colour

and friable after a time. This ultimate product of the decomposition of guncotton has been found to contain glucose and oxalic acid in considerable proportions, besides a gum-like substance, formic acid, cyanogen, and an organic acid which by some observers is considered to possess novel characters. Divers believes that he has identified pectic and parapectic acids in the product of a decomposed specimen. The amorphous mass has also been found to evolve ammonia when heated with a solution of potassium hydroxide. In some instances the guncotton is described as having undergone other intermediate changes, but the greatest discrepancies exist between the observations of even the most practised experimenters regarding the periods within which the decomposition of guncotton has become manifest, and the conditions under which the changes have occurred. In some instances the first signs of decomposition were observed after exposure of the guncotton to daylight for several years, in others a few days' exposure sufficed to establish the change.

Some observers state that the material has been preserved in the dark for very protracted periods without change, others (*e.g.* quite recently De Luca and Blondeau) show that, even in the dark, guncotton undergoes decomposition within a comparatively short period. Such conflicting observations afford convincing proof of great variations in the composition or degree of purity of the materials experimented upon. The exposure of guncotton to heat has, by most observers, been found to accelerate its decomposition considerably; but here again great discrepancies are presented by different accounts of the behaviour of the material under the influence of different temperatures; thus, spontaneous explosion has been brought about in some instances by brief exposure to a degree of heat which, in others, has only produced a comparatively very gradual decomposition. The most interesting and important of recent observations upon the influence of heat on the stability of guncotton, are those described by Pelouze and Maury in their recent report upon Baron von Lenk's system of manufacturing guncotton, and upon the composition and properties of the products which it furnishes. They describe a number of results obtained with specimens of guncotton which, it is to be inferred, were all produced according to von Lenk's directions, and which, therefore, provided these

were strictly adhered to, and such an adherence ensured the uniformity of the products, should have furnished reliable data regarding the powers of purified guncotton to resist the destructive effects of heat.

The principal results arrived at by Pelouze and Maury are as follows. They found that all specimens which were heated to 100° C. became decomposed in more or less time; a few minutes' exposure to that temperature sufficed in every instance to determine the evolution of nitrous vapours. They describe the results of decomposition as susceptible of variation at will; either the guncotton might be brought to explode, or the various forms of decomposition already described by other chemists might be established; or finally, it might be made to furnish simply a small black residue presenting the appearance of carbon, from which ammonia might be disengaged. Identically the same results were obtained by exposing specimens of guncotton to temperatures of 90° and 80° C. with this difference, that the phenomena of decomposition, instead of appearing in a few minutes, were not exhibited until after the lapse of several hours. It is further stated that pyroxylin is decomposed at 60° C., and even at 50° C.; after the lapse of several days dense vapours filled the vessel containing the specimens, but no explosions of guncotton occurred in the experiments conducted at those temperatures. Great stress is laid, however, upon an instance of explosion which occurred with a specimen of guncotton prepared according to von Lenk's process, immediately upon its coming into contact with the metal of an oil-bath, the temperature of which was only 47° C. at the time. Pelouze and Maury afterwards refer to the instances of spontaneous decomposition of guncotton at ordinary temperatures observed by other chemists, and to certain specimens, among a number prepared at Bouchet in 1847, which had undergone alterations such as have already been described. These were examined for sulphuric acid, and none was detected; hence the conclusion is drawn that these samples had been perfectly washed, and that their spontaneous change could not be ascribed to imperfect purification. It is argued that instances of change have been observed to occur under ordinary atmospheric conditions, similar to those established in guncotton at higher temperatures; that, because exposure to the latter had occasionally brought about spontaneous explosion, it is possible for instances of

spontaneous decomposition at *ordinary* temperatures to result in explosions, and that, consequently, it is right to conclude that the storage of large quantities of guncotton is attended by great risk of explosion. In further support of this conclusion, the observations are recorded, that the most perfectly washed guncotton becomes acid by long exposure to sunlight; that some pyroxylin, which was alkaline at first, after exposure for several weeks to light, in contact with the sides of a glass flask, exhibited an acid reaction; and that, even when guncotton is preserved in the dark, this acidity invariably becomes manifest in course of time. Finally, without referring to any single instance in which an explosion or even an appreciable development of heat has been observed as resulting from protracted exposure of guncotton to strong daylight or sunlight, Pelouze and Maury conclude that the indications of gradual decomposition furnished by certain specimens of guncotton under those conditions, are sufficient proof of the liability of this material, as now manufactured, to explode spontaneously, when stored in considerable quantities.

The researches into the manufacture, composition, and properties of guncotton, upon which, as a member of the Government Guncotton Committee, I have been engaged for nearly four years, have included, from their very commencement, careful observations and a great variety of experiments, with both small and large quantities of material, bearing upon the influence exerted by light and heat, and by various modifications introduced into the system of manufacture, upon the stability of guncotton produced in accordance with the general directions laid down by von Lenk. It is obvious that, although most of these experiments have furnished very decisive results within a comparatively brief period, there are others which become the more valuable and the more fully conclusive in their character, the longer the period of their duration. It is considered, however, that the data which even the latter class of experiments has already furnished possess sufficient scientific interest and practical importance to warrant their present publication, in addition to those obtained by numerous experiments instituted with the view to ascertain whether, and to what extent, the results of researches recently published in France upon the spontaneous changes of guncotton, apply to the

material manufactured in this country during the last four years.

The experiments and observations carried on at Woolwich may be classed as having for their objects:—(a) The determination of the influence of light and of long protracted storage, under ordinary conditions as to temperature, upon the stability of guncotton. (b) The investigation of the behaviour of guncotton upon exposure, under varied conditions, to artificial temperatures, and to such elevated natural temperatures as are occasionally experienced in particular localities. (c) The examination of the influence exerted upon the stability of guncotton by special modes of preparing and preserving it.

A few observations have been made upon specimens of guncotton which either were prepared by myself or came into my possession previous to the commencement of the present inquiry, but all actual experiments have been instituted with samples of products of manufacture obtained at Hirtenberg, Stowmarket, and Waltham Abbey, some modifications having been introduced, in special instances, in the ordinary system of operation at the last-named manufactory, with the view of ascertaining the nature and extent of their influence upon stability.

CHAPTER XIV

ABEL ON THE ACTION OF LIGHT AND HEAT UPON GUNCOTTON (1867)¹

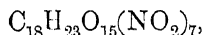
THE want of uniformity in power to resist the destructive action of light, exhibited by different specimens of guncotton with which chemists have experimented, has been additionally exemplified by the behaviour of numerous specimens of guncotton which have from time to time come into my hands, or were prepared by me, previous to 1862. I will limit my notice of such specimens to two examples.

In the autumn of 1846 a small quantity (one or two pounds) of guncotton was prepared by me at the Royal College of Chemistry according to directions which had been made public in Germany a short time previously. The product, which was insoluble in mixtures of ether and alcohol, was obtained by immersing carded and purified cotton-wool of very high quality for a few minutes in the prescribed mixture of nitric and sulphuric acids, afterwards exposing it for several hours to a current of water, then digesting it in a cold dilute solution of potassium carbonate, and finally washing it in pure water. The larger proportion of the product was gradually expended in lecture experiments, but a specimen has been preserved by me up to the present time. For sixteen years it was simply enveloped in paper and kept in a drawer much used; at the expiration of that period, when it was found to be perfectly unchanged, not exhibiting the slightest acidity or odour, it was transferred to a stoppered bottle, in which it has been since exposed to diffused daylight for four years. This specimen still remains perfectly unchanged.

Messrs Hall of Faversham had the goodness, about three and a half years ago, to disinter at my request a sample of a large quantity of guncotton manufactured by them in 1847, and which they buried upon the occurrence of the disastrous explosion at their works in that year.

¹ *Trans. Roy. Soc.* (1867), 181-253.

This sample was much discoloured when received, but the fibre was strong, and the material did not appear to have undergone any change. Its explosive properties were, however, considerably inferior to those of guncotton prepared according to Schönbein's or von Lenk's directions; and, upon analysis, it furnished results corresponding very nearly with those required by the formula



or collodion guncotton, of which the composition was determined by Hadow. It was, moreover, readily soluble in a mixture of ether and alcohol, and furnished a good collodion film. It is most probable, therefore, that a deficiency in the strength of acids employed in its production had led to the manufacture, in this instance, of soluble and less explosive guncotton by Messrs Hall.¹ A specimen of this material, after having been very carefully washed, was dried and enclosed by me in a stoppered bottle, in which it has remained exposed to diffused daylight for upwards of three years. A piece of litmus paper, enclosed with the guncotton, exhibited faint signs of reddening within three months after the first exposure, and within twelve months it was bleached. At this time the guncotton possessed a faint but decided cyanic odour; no nitrous vapours were perceptible within the bottle, either then or at any more recent period up to the present time, though the odour of the guncotton has now become more pronounced, and is indicative of nitrous acid. The substance has at present a marked acid reaction; it has not as yet altered either in explosiveness, strength of fibre, or other properties, but the odour and slight development of acid are undoubted indications that the material which for sixteen years was preserved in a moist condition in the dark without any apparent change, has during three years' exposure to light furnished slight indications of a

¹ The author communicated to the Seventh International Congress of Applied Chemistry in London in 1909 the results of the analysis of a sample of the guncotton mentioned by Abel. It had been standing in a stoppered bottle in the office of Messrs John Hall & Sons, Faversham, for a great number of years. It was in excellent physical condition, and had been made from fine cotton-wool. The following were the analytical details:—Nitrogen, 11.95 per cent.; solubility in ether-alcohol, 89 per cent.; heat test at 170° F., 27 minutes; stability test at 135° C. (with 0.25 grm.), faint fumes, 11 minutes, strong fumes, 20 minutes; did not explode in 1 hour; solubility in ether in soxhlet, 4.8 per cent.; ash, 1.27 per cent.; insoluble in acetone, 1.44 per cent.; solubility in cold absolute alcohol, 14.79 per cent.

spontaneous change. It was a specimen of guncotton prepared by Messrs Hall in 1847, and preserved by Percy since that year in a stoppered bottle, exposed to light, which had gradually become converted into a light brown semi-fluid gum-like mass, described by Hofmann as having exhibited all the properties of ordinary gum, and as being interspersed with crystals of oxalic acid. It is therefore not improbable that the specimen of Messrs Hall's manufacture, above referred to, may, by long-continued exposure to light, eventually furnish more important indications of spontaneous change than have hitherto been developed in it. There can be little doubt that the quality of the cotton operated upon by Messrs Hall in the production of the specimens above referred to (and certainly in the instance of that examined by me), was considerably inferior to that of the material employed by me in 1846, and the character of the guncotton produced demonstrates that the conditions essential to the production of the most explosive material were not fulfilled by the method of manufacture pursued by those gentlemen in 1847. It is equally certain that the great importance of as complete a purification as possible of the cotton employed and of the product obtained was not fully recognized at that period, and that consequently, although a small laboratory operation, carefully conducted according to the prescribed directions, might furnish a pure product of great stability, the operations of manufacture had not been established with the precision essential to the attainment of satisfactory results.

The following are the results obtained up to the present time by exposure to light, under various circumstances, of guncotton prepared and purified according to von Lenk's directions. Exposure to strong daylight and to sunlight, either in the open air or in a confined space for a few days (two or four), develops in the guncotton a very faint aromatic odour; and if litmus paper be allowed to remain in close contact with the confined material, it acquires a rose-coloured tinge similar to that produced by carbonic acid, and recovers its original colour after brief exposure to air. If, after exposure to light in open air for some days, the guncotton be placed in the dark, in cases which are not air-tight, the odour becomes gradually fainter, and the effect upon the litmus paper slighter; if the packages containing the guncotton are air-tight, the odour and action upon litmus do not increase during storage for several years

(the actual experience gained at Woolwich extends over nearly four years).

If the guncotton be exposed for protracted periods to daylight with free access of air, it speedily loses all odour and power of affecting litmus. If exposure to diffused daylight in a confined space be continued, the first results of the action of light are, of course, retained; but up to the present time no single indication of their increase has been observed; indeed, the very faint acid reaction described, which was developed at first, has frequently disappeared, probably in consequence of the neutralizing action of small quantities of earthy carbonates contained in the guncotton. But if the material be exposed continuously in a perfectly confined space to the action of sunlight or strong daylight, it furnishes, after a time, much greater evidence of change than that already described. The acidity gradually becomes more manifest; the odour increases, and becomes in time somewhat pungent and indicative of the presence of very small quantities of nitrous acid; and litmus paper, if confined in the vessel with the guncotton thus exposed, becomes entirely bleached after two or three months. Although specimens of guncotton always undergo some spontaneous change under these very special circumstances, the decomposition proceeds with extreme slowness; and the results of the observations instituted by me are therefore, in this respect, quite at variance with those recently published by De Luca, who states that the specimens operated upon by him decomposed upon exposure to sunlight, some on the first day of the experiment, others after several days' exposure.

Experiments showed that (1) guncotton in an ordinarily dry condition undergoes very slow change indeed, when freely exposed in closed vessels (either containing air or with air excluded) to strong daylight and to the light and heat of the sun, the effects upon the material, during upwards of three years' exposure, being to diminish its explosiveness somewhat by the reduction of a portion of the trinitrocellulose to lower cellulose products. The material, when purified by washing in alkaline water after this very severe exposure to light, is still guncotton possessing useful explosive properties, and exhibiting no greater tendency to change than the original material. (2) If the space in which the guncotton is enclosed be kept saturated with aqueous vapour, the substance under-

goes decidedly more rapid and considerable change, though, even under these circumstances, guncotton prepared according to the system now in use is much less rapidly decomposed by severe exposure to light than has been the case with specimens of guncotton previously experimented upon. Samples of guncotton which had been submitted to a less perfect purification than usual, afforded indications of being somewhat more rapidly affected by prolonged exposure to strong daylight and sunlight. Experiments which proved that the preservation of guncotton in an atmosphere saturated with moisture rendered it somewhat more prone to alteration by long-continued exposure to light, have been confirmed by other experiments still in progress, in which known quantities of moist and wet guncotton are exposed to light in confined spaces, in comparison with dry guncotton. Thus, in one of these experiments, perfectly dry guncotton and guncotton in a damp condition have been enclosed in large stoppered bottles and exposed side by side to strong daylight and sunlight. After the lapse of two (summer) months they were carefully dried and their weights determined. The sample which had been exposed, saturated with water, to light had lost 0.33 per cent.; the weight of the dry sample indicated a loss of only 0.02 per cent. They were then again exposed in the wet and dry condition for four months; the total loss in weight of the sample exposed in a wet condition was then found to amount to 0.6 per cent.; that of the dry sample only to 0.14 per cent. (after six months' exposure). A trifling oxidation at the expense of oxygen in the water, established by the agency of sunlight, is doubtless the cause of the slight but decided influence which, under these circumstances, water has been observed to exert upon the permanence of guncotton; an influence which is quite opposed to that exerted by the presence of water on guncotton stored in the dark, or exposed to high temperatures, as will be presently demonstrated.

The statement made by De Luca that when once decomposition has been established in guncotton, resulting in the development of nitrous acid, the progress of the change cannot be arrested, is not borne out by the results of numerous observations made by me. Many specimens of guncotton which, by exposure to high temperatures (100° and 90° C.), or by very long-continued exposure to lower temperatures (50° to 65° C.), have suffered considerable change, resulting in the development

of nitric peroxide and of other products, have been afterwards preserved in glass bottles, both tightly closed and partially open, and freely exposed to light for periods ranging from one to three years, without undergoing additional change. In a few exceptional instances, further decomposition has after a time been established by the influence of light; but in those the guncotton was impregnated to a considerable extent with free nitric acid. Such specimens, in case they were then thoroughly washed (a slightly alkaline solution being employed in their first purification), have afterwards not been found, up to the present time, to exhibit any greater tendency to decomposition, by exposure to light, than the original guncotton.

Effect of Heat upon Guncotton.—The behaviour of guncotton under exposure even to comparatively high temperatures is subject to very considerable modifications, which may be in great measure determined by the conditions of treatment. Illustrations of this were obtained at an early period of these investigations, in experiments instituted with the view of ascertaining the average temperature at which guncotton explodes.

Exploding Point of Guncotton.—The apparatus employed in the experiments on this subject consisted of a small air-bath fitted with a thermometer and closed with a mica plate, having a little circular opening in the centre, through which the guncotton might be introduced, and which was kept closed when not in use. The mode of operating was modified in various ways. In the first instance the guncotton was combed out into a very loose condition, and allowed to rest upon metal in the air-bath. The temperature of the latter was then raised very gradually from 15° C. to 204° or 205° C. When the time occupied in the passage to the maximum temperature was two hours and upwards, the guncotton did not explode at all (in six experiments), but gradually became dark brown, quite friable, and deprived of all explosive properties. When a considerably shorter time (about one hour) was occupied in the attainment of the maximum temperature, the guncotton exploded on one or two occasions, but not until its temperature had reached 205° C. In the next experiments, the guncotton was employed in very small compact masses, and, resting upon a wooden support, was exposed to a continuously increasing temperature. The passage from 15° C. to the exploding point ranged, in these experiments, from forty-five minutes to two hours. The results obtained varied

between 136° C. and 138.5° C. Another series of experiments was instituted for ascertaining in what particular mechanical condition the guncotton exploded most readily, and at most uniform temperatures; and ultimately the material was employed in the form of pieces of loosely-twisted strand about 20 mm. long, and its exploding point was determined by first raising the atmosphere of the air-bath to 105° C., then allowing the specimen to fall upon a diaphragm of wire gauze in the air-bath, at once increasing the temperature as rapidly as possible, and carefully reading the thermometer until the explosion occurred. The result of eight observations varied between 147° C. and 151.5° C. These last experiments, which appear the most trustworthy, indicate that the average temperature at which the guncotton explodes, when in a condition most favourable to its rapid heating, is about 150° C. In two observations, in which the guncotton was in a very open condition, the temperature being raised more rapidly than usual, the explosions occurred when the thermometer indicated 145° and 143.5° C.; and in the experiments preceding these, which were differently conducted, compact guncotton being exposed to heat for a considerable time, the point of ignition ranged between 136° and 138.5° C. Schrotter, Redtenbacher, and Schneider, in their report upon von Lenk's guncotton, mention that 136° C. is the *lowest* temperature fixed by von Edner at which this material explodes.

CHAPTER XV

ABEL ON HEATING GUNCOTTON TO 100° C. (1867) ¹

PELOUZE and Maury, in their accounts of the effect of heat upon guncotton, describe several kinds of stages of decomposition as occurring, or producible at will, by its exposure to a temperature of 100° C., and state that in every instance they found a few minutes' exposure to that temperature sufficient to produce a disengagement of nitrous vapours. A large number of experiments have been instituted with guncotton prepared at Waltham Abbey and Stowmarket according to von Lenk's direction, and also with some specimens of Austrian guncotton, with the view of ascertaining the effect upon them of exposure to 100° C. The guncotton was exposed to heat in sealed tubes and in open vessels arranged in different ways. The quantities operated upon and other conditions in the experiments were varied, as will be presently particularized, the objects contemplated being, in the first instance, to examine into the effects of exposure of guncotton to heat, and afterwards to ascertain if possible by what circumstances those effects might be subject to modification.

Experiments in Sealed Tubes.—Air-dry guncotton (coarse yarn, manufactured in 1863), enclosed in a stout glass tube hermetically sealed, was maintained at 100° C. in a water-bath. The tube was filled with deep orange vapours in about three hours. The vapours gradually diminished in intensity, after a time, until the guncotton was converted into a gum-like mass, the transformation occurring most rapidly at the upper end of the tube, where the water produced during the change condensed and returned, charged with acid, upon the guncotton. When the sealed tube was opened, after continuation of the heat for three or four days (seven hours daily), nitric oxide escaped under considerable pressure. Upon closing the tube again, after the escape of gas, and continuing the application of heat, the guncotton was gradually converted into a black

¹ *Trans. Roy. Soc.* (1867), 181-253.

pitch-like mass. This experiment, several times repeated, always furnished closely similar results. A tube containing fine guncotton thread, manufactured in 1863, was exhausted and sealed. After four hours' exposure to 100° C., it exploded with great violence, tearing open the stout copper water-bath in which it was heated. Portions of unburned guncotton were scattered about.

Another tube, containing some of the same guncotton, was opened after seven hours' heating, to allow the gas to escape, and again sealed. On the second day, after heating for three or four hours, it exploded violently. Several experiments were made with perfectly dry guncotton, and furnished results quite similar to those obtained with the air-dry material. Fine guncotton thread was introduced into a tube sealed at one end; the other extremity of the tube was constricted, then exhausted and filled with nitrogen, these operations being repeated three times; the tube was afterwards filled and heated to 100° C. in a water-bath. After forty-five minutes faint red vapours were observed. In another quarter of an hour the colour of the vapours was very deep; in a short time nitrous acid began to condense in the cool part of the tube. After continuing the heat for $1\frac{1}{4}$ hours longer, the coloured vapours had entirely disappeared. The guncotton had become highly bleached, and in the upper extremity of the tube it was partially converted into a gummy substance. Nitric oxide escaped when the tube was opened. A sample of guncotton impregnated with about 0.4 per cent. of alkaline carbonate was exposed to 100° C. in an exhausted sealed tube, for the purpose of collecting the gases evolved. When the tube had been heated six hours daily for five days, it was opened under mercury, and the gas, which escaped under considerable pressure, collected. The tube was again closed and heated for two days, when gas was once more collected from it. The experiment was interrupted, after the guncotton had been further heated for two days, the tube being fractured by the effects of an explosion in its vicinity. The collected gases were found to consist of 50.2 per cent. of carbonic acid, 4.7 per cent. of nitric oxide, and 45 per cent. of nitrogen. These experiments, in which the guncotton was submitted to the influence of 100° C. under the most severe conditions, appear to indicate that nitric peroxide or nitrous acid is liberated by the first decomposition of the guncotton, and at once establishes

a further destructive action upon the substance, becoming reduced to nitric oxide, nitrogen being eventually liberated by complete reduction of the latter. The extent of surface of guncotton presented to the action of heat and of the liberated acid appears to exert, as might be anticipated, an important influence upon the change. Exposure of fine guncotton thread to heat under the same conditions as those which were safe with coarse yarn gave rise to explosions, due possibly to the increased pressure of gas in the tubes, but more probably, judging from their great violence, to the sudden decomposition of the guncotton at a particular period. The characters exhibited by the products of decomposition of guncotton obtained in these experiments were similar to those already described by other chemists, and have been referred to previously.

Experiments in Vessels open to the Air.—The following experiments, conducted with considerably larger quantities of guncotton than before employed, were made with the view of obtaining at one time several distinct data regarding the decomposition of guncotton at 100° C. Direct evidence was sought of the development of heat in guncotton upon continued exposure to that temperature. The period was carefully noted when decomposition was first indicated by the disengagement of nitrous acid, after commencement of the experiment. In some instances, the loss of weight sustained by the guncotton was determined at intervals (*e.g.* at the close of six hours, or one day's exposure to heat), the nitrous acid contained in the vessel being first displaced. The vessels employed in these experiments were globe flasks fitted by means of perforated corks with long narrow glass tubes, and in most instances with thermometers graduated from 100° C. upwards. The flasks were of a size to receive the guncotton in a compact condition, and the thermometer bulbs were inserted into the centre of the mass. Continuous observations were made in safety during the experiments, through a small glass let into a wooden screen, which was placed in front of the water-bath containing the heated flask.

The results indicated: (1) That sufficiently protracted exposure to 100° C. under conditions unfavourable to the rapid expulsion of the nitrous acid developed by the first action of the heat upon the guncotton, ensures the complete destruction of the original properties of this substance, and its con-

version into a variety of volatile and fixed products. (2) That the rapidity and violence of the decomposition resulting from the combined action of heat and of the acid generated, is regulated by the quantity of guncotton operated upon. (3) That, as shown by experiments conducted with coarse and fine yarn manufactured in precisely the same manner, the mechanical condition of the guncotton exerts an important influence over the rapidity of decomposition at 100° C. (a point also indicated by the results of experiments in sealed tubes). (4) That a very important difference may exist between the behaviour of different samples of guncotton, even if operated upon in precisely the same manner, quantities, and mechanical conditions.

This is illustrated by comparing experiments (conducted with Austrian guncotton) with precisely similar experiments instituted with different samples of Waltham Abbey guncotton, in not one of which was an explosion brought about by long-continued exposure of equal quantities (6·5 grms.) to 100° C. The two specimens of Austrian guncotton differed very greatly in composition from all the products of manufacture prepared at Waltham, according to von Lenk's system; and it will be shown presently that this circumstance may serve to account for the exceptional proneness of these specimens to very violent decomposition under the particular conditions of the above experiments. It need perhaps scarcely be stated that the temperature observations in these experiments (and others still to be described) were instituted more with the view to afford a good means of registering the comparative rapidity of decomposition of different specimens of guncotton operated upon under equal conditions, than with the idea of attempting to ascertain the actual moment of development of heat and progressive rise of temperature in a mass of guncotton. Such observations could only be correctly made with much larger quantities of guncotton, so confined as to prevent the escape of heat from the interior, and are therefore impracticable on the score of danger. A considerable number of these thermometric observations, which unquestionably recorded close approximations of the actual rise in temperature of the interior of the mass of badly-conducting guncotton, showed that when the temperature passes 110° to 112° C., the development of heat proceeds with great rapidity, so that very speedily the rise of the thermometer

does not keep pace with the heating of the portions of the guncotton in close proximity to it, and therefore the explosion of the mass appears to occur at a temperature considerably lower than the actual exploding point of guncotton.

In continuation of the heat experiments, several samples of guncotton from Waltham Abbey and Stowmarket, weighing 3 grms. each, in an air-dry condition, were exposed to 100° C. in conical assay flasks, into which long quill-tubes were fitted. Eight experiments conducted precisely alike pointed to a very important difference in the powers of different specimens of guncotton to resist destruction by exposure to 100° C. Of five samples manufactured at Waltham Abbey, only one exhibited the effects of such exposure described by Pelouze and Maury as invariable, namely, the disengagement of nitrous vapours within a few minutes. One specimen did not exhibit this sign of change until after five hours' exposure, and then only to a very slight extent. Of two specimens of guncotton from Stowmarket, one decomposed with very considerable rapidity at 100° C., and the other did not, in one experiment, evolve any visible amount of nitrous acid during forty-five hours' exposure in nine days, and exhibited very slight signs of change at the expiration of this severe treatment; while in a second experiment, with a portion of the same sample, slight decomposition became apparent at the close of the third day's exposure of five hours. The cause of the latter difference in the behaviour of one and the same sample, upon different occasions, was traced to the circumstance that the specimen, in the condition in which it was first employed, contained a somewhat larger proportion of moisture than when the experiment was repeated with it, in consequence of its having been in a damp locality for a short time before the first portion was operated upon. Thus one possible reason for the different behaviour of several samples of guncotton prepared by one and the same process was indicated. In confirmation of the influence exerted by moisture in retarding the decomposition of guncotton exposed to a high temperature, the results of a preliminary experiment may be here recorded, which was instituted with a sample of guncotton found to be very readily affected by exposure to heat. Three specimens, each of 1 grm., were exposed side by side in small long-necked flasks to 100° C., in three different conditions. The one was air-dry (and contained therefore about 2 per cent. of

water), the second was dried immediately before the experiment by sufficient exposure to 50° C., and the third was saturated with water and pressed between bibulous paper. The dry sample showed signs of decomposition in ten minutes, the air-dry sample began to decompose in forty-five minutes, and the moistened specimen exhibited no acidity after exposure to 100° C. five hours daily for three days. Further experiments on the protective power of water will be presently described. In all subsequent experiments upon the comparative effects of exposure of different samples to elevated temperatures, the guncotton was employed in a dry condition.

It has been argued by Schrotter, Redtenbacher, and Schneider in their official report upon von Lenk's guncotton, that an incomplete conversion of cellulose into the most explosive guncotton may be one cause of the want of stability observed in the early products of manufacture (at Bouchet, etc.); and consequently the existence in guncotton of partly nitrated cotton should, according to some chemists, give rise to, or promote a tendency to spontaneous change in the material. On the other hand, Pelouze and Maury consider it probable that a guncotton will be the more liable to spontaneous change the further it is removed in composition from the cellulose type, and that products prepared by prolonged immersion in large proportions of very concentrated acids will therefore be more liable to spontaneous ignition than the guncotton prepared by a brief immersion in less concentrated acids. No experimental data are given in support of either opinion. The discordant results furnished by the heat experiments just described, and the facts established by investigating the composition of the guncotton operated upon, led to the institution of a very considerable number of experiments with the view of ascertaining, if possible, whether the establishment of change in guncotton by its exposure to high temperatures has to be ascribed to the instability of trinitrocellulose itself, or whether it is to any extent ascribable to the injurious influence of less permanent bodies existing as impurities in the ordinary product of manufacture. A carefully comparative examination was instituted on the effects of exposure, under equal conditions, to 100° C. upon a number of samples in portions of which the matter soluble in ether and alcohol had been determined. One gramme of each sample was first dried in a water-bath

at a temperature of 50° C.; it was then introduced loosely into a small flask having a neck about 220 mm. in length, and immersed in boiling water, the first indication of the disengagement of nitrous acid being afterwards carefully noted. The specimens were uniformly exposed to 100° C. for thirty hours (six hours daily for five consecutive days), unless, as was the case in a few instances, the guncotton had suffered complete change within a shorter period.

The results show that different samples of the material, manufactured as far as possible in the same manner, are not alike affected by exposure under uniform conditions for a fixed period to 100° C. Of thirteen samples of Waltham Abbey guncotton, four resisted in a remarkable manner the destructive effects of heat, and remained unchanged in physical properties and explosiveness after thirty hours' exposure to 100° C. This treatment only developed acid to a slight extent in these samples; but in the other nine specimens it produced somewhat greater alterations; nitrous acid was disengaged in more considerable proportions, the fibre of the guncotton was rendered more or less rotten, and its explosiveness was diminished in different degrees. The comparative celerity with which nitrous acid is disengaged from different specimens of guncotton upon exposure to 100° C., does not afford a reliable indication of their relative susceptibility to rapid decomposition at that temperature. A careful examination into the possible causes of these differences showed that they were to be ascribed, at any rate in very great measure, to variations in the proportion and character of the mineral matter contained in the specimens. Some few of the Waltham Abbey samples contained larger proportions of calcium and magnesium carbonates (deposited upon the fibre by the hard water in which the material had been washed) than other samples. There was consequently present in such specimens a larger amount of matter capable of neutralizing acid, if liberated by the action of heat, than in others; and therefore the period would be proportionately delayed, in those instances, when the development of free acid would first become evident. The Stowmarket samples had been submitted to the "silicating" process, which consists in impregnating the guncotton with a dilute solution of soluble glass, afterwards drying it, and finally washing it in spring or rain water. The result of this treatment

is that small proportions of alkaline and earthy carbonates are deposited upon the fibre in addition to what it would acquire by simple long-continued exposure to running water. This circumstance tends to explain why the Stowmarket guncotton experimented with, though generally much more seriously affected by protracted exposure to 100° C. than the Waltham Abbey samples, appeared to resist change in several instances for much longer periods than the latter. The proportion and nature of the mineral matter in guncotton may, therefore, as shown by those experiments, exert a very notable effect upon the behaviour of the material when exposed to high temperatures. But the results of subsequent experiments have demonstrated most decisively that the influence which the presence of earthy or alkaline carbonates, mechanically distributed in small proportion through a mass of guncotton, exerts upon the effects produced by exposure to heat, is in many instances not confined to a simple delay of the indications of change furnished by the development of acid; it may also manifest itself in much more important directions, namely, by actually retarding and even considerably limiting, if not altogether preventing, the spontaneous decomposition of the guncotton itself. These effects are of such evident importance in connection with the question of the stability of guncotton, that they have been made the subject of extensive experimental inquiry, the results for which will be given under a special head.

The different behaviour of the samples of guncotton operated upon in the foregoing experiments cannot be ascribed to differences in the proportions of matter soluble in ether and alcohol present in them. The want of connection between the proportion of matter soluble in ether and alcohol, and the stability of the sample, is perhaps even more strikingly demonstrated by results obtained with specimens of Stowmarket and Hirtenberg products. A comparison of the general results furnished by the Waltham Abbey and Austrian samples might be considered to afford some foundation for the conclusion that the guncotton which contains the largest proportion of the less explosive cellulose products is the most susceptible of change, but it has already been shown that this conclusion is not supported by comparison of the individual experiments; and the following additional illustrations may be pointed out. A sample of Waltham Abbey

guncotton containing 1·83 per cent. of soluble matter sustained decidedly greater change than Austrian samples containing 4·5 and 5·02 per cent., or than a Stowmarket sample containing 8·5 per cent.; and a specimen of Austrian cotton containing 3 per cent. of soluble matter did not sustain less alteration. and was much more rapidly affected than one from Stowmarket containing 11·78 per cent. Again, the specimen of Austrian guncotton, which consisted chiefly of the lower nitro-products, was not so rapidly or completely changed as another Austrian specimen which contained only 7·4 per cent. of soluble matter or a Stowmarket sample which contained but 4·3 per cent.

A comparison of the characters exhibited by the matter which ether and alcohol extracted from different samples employed in these experiments, appeared to throw much greater light upon the causes of their different behaviour than the comparison of the proportions of soluble matter which they furnished. Reference has already been made to the matter soluble in alcohol alone, which has been discovered in small but variable proportions in all samples of guncotton hitherto examined. Both the quantity and character of these substances extracted from different specimens of guncotton exhibit variations, as might be anticipated, when it is remembered that they are derived from impurities retained by the cellulose, to an extent determined by the particular description and degree of purity of the cotton operated upon. In the Waltham Abbey specimens employed, the proportion of matter varied only slightly (between 0·72 and 0·9 per cent.); yet, although the comparatively slight differences in the effects of heat upon the different samples were in part ascribable to variations in the proportions of mineral matter present, indications were obtained that the guncotton which resisted the action of heat to the greatest extent contained the smallest proportion of nitrogenized organic matter not derived from cellulose. The Stowmarket samples afforded much more decided evidence of the influence of these foreign products upon the stability of the guncotton. Two specimens from which nitrous acid vapours were disengaged within ten minutes of their first exposure to 100° C., and three others which, owing apparently to the influence of mineral matter, did not furnish acid vapours until after five hours' exposure, yielded extracts with ether and alcohol decidedly different in character from the other specimens; a comparatively large proportion consisted

at once removed from the liquid and dried. The mechanical condition of the guncotton was not perceptibly altered by the treatment. These specimens were exposed to 100° C., together with portions of the original samples (all of them being for this purpose packed lightly and uniformly in small flasks). In every instance the prepared guncotton resisted the action of heat for a much longer period than the unprepared material. The former exhibited the first very faint indications of the disengagement of nitrous acid between twelve and fourteen hours after the first exposure, while the unprepared specimens evolved nitrous acid after one hour to one hour and thirty minutes' exposure. The addition of less perfectly converted guncotton to the ordinary product does not have the effect of promoting its decomposition at 100° C., but, on the contrary, when applied as indicated above, it renders the material considerably less susceptible to change, probably because the fibres are partially sealed, or in some other way mechanically protected by the treatment with dilute collodion.

That the partial or complete closing of the fibre does exert an important influence upon the power of guncotton to resist the action of heat was demonstrated by allowing guncotton to remain for eighteen hours in a confined space together with an open vessel containing ether and alcohol. It was afterwards dried and exposed to 100° C., side by side with a portion of the sample in its original condition. The latter exhibited signs of decomposition within two hours, but the sample which had been exposed to the action of the vapour only exhibited faint signs of change after eighteen hours' exposure.

The following conclusions were drawn:—(1) That the invariable existence in guncotton of small proportions of organic impurities resulting from the partial oxidation of foreign matter enclosed within the cotton fibre exerts a very prejudicial influence upon the stability of trinitrocellulose. (2) That there is no sound foundation for the opinion that any such influence is exerted by the lower cellulose products when associated in large or small proportions with trinitrocellulose.

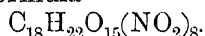
CHAPTER XVI

ABEL ON HEATING GUNCOTTON TO 50°-60° C. (1867)¹

THE air-dry guncotton was introduced into large bulbs blown at the extremities of barometer tubes, the latter being placed with their openings over mercury and exhausted in the manner already described, so that the height of the mercury column in these tubes, at the commencement of the experiments, was very nearly that of the barometer at the time. Sufficient guncotton was employed to fill the globes pretty compactly. The bulbs were enclosed in metal water-baths, in which they were always perfectly surrounded by water maintained for definite daily periods at a constant temperature by gas flames, accurately adjusted by self-acting regulators. Daily observations were made, before heat was again applied, of the height of mercury in the tube (with the necessary corrections), of the appearance of the guncotton through the glass, and of any other points worthy of note. Guncotton, manufactured at Waltham Abbey in 1863, was heated for six days, seven hours daily, to a temperature ranging between 36° and 38° C. The column of mercury was not permanently affected to the slightest extent during this period. It was afterwards intended to maintain the temperature for a long period at 49° C., but upon the second day of this treatment the heat was accidentally raised to 55° C. It was therefore afterwards maintained at that point for a considerable period. After the first day of this treatment, the column of mercury continued to fall daily, to an extent ranging between 8 and 16 mm. during nine days further exposure for six hours daily to 55° C. For three subsequent days the column fell 18, 20, and 18 mm., on the thirteenth day the fall amounted only to 11 mm. On the fourteenth day the temperature rose accidentally to 60° C., and remained at that point about thirty minutes; on that day the fall of the mercury column amounted to 23 mm. The temperature was afterwards maintained at 55° C., but the daily depression of mercury did not correspond

¹ *Trans. Roy. Soc.* (1867), 181-253.

of nitrogenized acid matter of a resinous character, soluble in alcohol. With two or three exceptions, the samples of Austrian guncotton exhibited decided signs of less complete purification of the cotton previous to conversion than the generality of samples of English manufacture. It should also be observed that the extract by ether and alcohol, after treatment of the samples with alcohol alone, possessed in several instances the characters of photographic collodion (the solutions furnishing tough transparent films, upon glass), which was not the case with any of the specimens of Waltham Abbey guncotton, and in only one or two instances among the samples from Stowmarket. The ordinary ethereal extract from the English samples furnished a horny brittle residue, contracting greatly upon perfect desiccation, and appearing to consist chiefly of the product described by Hadow as having the formula



No decided evidence was obtained in support of the conclusion that this difference in the character of the ethereal extract affected the stability of the guncotton. On the contrary, the Austrian samples which did not furnish an extract having the properties of good collodion, and only yielded 7.5 and 8.5 per cent. of total soluble matter, decomposed far more rapidly and completely than the specimen which consisted chiefly of collodion guncotton. The destructive effect upon the structure of the fibre by the long-continued digestion of the guncotton in warm solvents, which is necessary for ensuring the extraction, as completely as is practicable, of the soluble matter, renders it very difficult to obtain reliable indications of the effects of heat upon guncotton deprived of those substances. The following experiments appear, however, to afford considerable support to the inference drawn from some of the results of the heat experiments just referred to, that the existence in guncotton of small proportions of organic impurities, resulting from partial oxidation of foreign matters enclosed in the cotton fibre, exerts a very prejudicial influence upon the stability of the material, and that there is no sound foundation for the opinion that any such influence is exerted by the lower cellulose products, when associated in small or large proportions with trinitrocellulose. Four specimens of guncotton, containing small proportions of imperfectly converted material, were thoroughly saturated with a very weak solution of pure soluble guncotton (or collodion), then

with the observations made before the temperature had accidentally reached 60° C. On three successive days it was 43 mm., 24 mm. and 37 mm. It appeared from these results that the increase of temperature to 60° C. had established a greater tendency to change in the guncotton, which afterwards continued, although the temperature was reduced to 55° C.

After this exposure of the guncotton to heat from six to seven hours daily for twenty-four days, during seventeen of which the heat applied was 55° C., and for a short time 60° C., the specimen was removed from the globe. It had not altered in appearance, but was found to be strongly acid to test paper; it had a peculiar pungent odour, the fibre had become tender, and its explosiveness had diminished somewhat. A portion of the specimen was washed thoroughly, first in distilled water and afterwards in slightly alkaline water, then dried and placed in a bottle, in which it has been exposed to diffused light for three years without undergoing further change. Nitrous acid vapours could not be distinguished in the globe or tube at any time during the experiment, but soon after the temperature was raised to 55° C. a few small yellowish crystals of mercurous nitrite appeared upon the surface of the mercury in the tube, and were added to a little as the experiment proceeded. Sixteen grms. of the sample of guncotton used in the preceding experiment, and 14.75 grms. of another sample, were exposed side by side, in one and the same water-bath, in the manner already described, to 55° C. for six to seven hours daily during seventy days. After the first day's heating the column of mercury in each tube was slowly and uniformly depressed, the volume of gas evolved being somewhat greater than from the second smaller sample. At the conclusion of seventy days' treatment it was calculated, from the capacity of the tubes and the amount of total displacement, that the larger sample had evolved 172.88 cc., and the other sample 189.1 cc. of gas; as, however, a few small crystals of mercury salt had been produced in each tube by the action of the nitrous acid disengaged, those quantities are of course only approximate. Upon removal from the bulbs, the colour of both specimens was unchanged; their odour was decidedly less pungent than that of the preceding specimen; both were acid to test paper, the smaller sample being the more strongly so; in neither instance was the strength of fibre im-

paired, the explosiveness diminished, or the solubility in ether and alcohol appreciably increased. The specimens were divided, put into stoppered bottles without any previous purification, and one bottle of each was preserved in the dark, the other being exposed to diffused light. None of the specimens have up to the present time (a period of $3\frac{1}{2}$ years) undergone any further change.

Fourteen grms. of guncotton were exposed in an exhausted bulb tube, as already described, to 65° C. for six to seven hours daily during a period of three months (eighty-four days). The depression of the mercury proceeded uniformly but much more rapidly than in the preceding experiment. After several days' exposure, a notable quantity of mercurous salt was deposited in crystals within the tube. At the termination of the experiment the guncotton was not altered in colour and appearance, but upon removal from the bulb the fibre was found to be considerably weakened; a pungent odour and strong acidity were exhibited by the specimen, its explosive properties were notably reduced, and it dissolved to a large extent in ether and alcohol, the solution furnishing a collodion film. A portion of the same guncotton enclosed in a smaller bulb tube, sealed at both extremities, was exposed to heat for an equal period in the same water-bath. There was some pressure of gas upon opening the tube, and the guncotton exhibited the same appearance and properties as the sample heated over mercury. Both samples were placed in closed glass vessels, and have since been exposed to light for upwards of three years, without undergoing any further change.

Four specimens of guncotton, each weighing 19·5 grms., taken from different samples, were introduced into bulb tubes of almost the same capacity and with stems of equal length. The bulbs were all enclosed in one water-bath, and the open extremities of the tubes were immersed in a mercury bath, over which they were exhausted, as in the preceding experiments. The water-bath was maintained at 65°, seven hours daily, the uniformity of the temperature being ensured by the employment of a self-acting gas regulator. Before commencing the application of heat each morning, the extent of depression of the mercury in the tubes was noted, and the volume of gas contained in each at stated periods was calculated from the observations made. The following were the conditions

of the samples after three months' exposure during seven hours daily to 65° C.

Waltham Abbey Fine Yarn.—Strong acid reaction; strength of fibre and explosiveness diminished. Aqueous extract contained nitric and oxalic acids, and reduced cupric salts readily. Proportion of matter soluble in ether and alcohol = 15 per cent.

Waltham Abbey Coarse Yarn.—Acid reaction; strength of fibre and explosiveness not appreciably diminished. Aqueous extract contained nitric acid and a trace of oxalic acid; reduced cupric salts to a very slight extent. Matter soluble in ether and alcohol = 49.1 per cent. (2 per cent. in original sample.)

Waltham Abbey Fine Yarn impregnated with 0.4 per cent. of Sodium Carbonate.—Strongly acid reaction; strength of fibre and explosiveness only slightly reduced. Aqueous solution contained nitric acid and a small quantity of oxalic acid; reduced cupric salts slightly. Soluble matter = 10 per cent.

Stowmarket Coarse Yarn.—Acid, friable; explosiveness very much diminished. Large proportion soluble in water. Solution contained a very small quantity of nitric acid but a large proportion of oxalic acid; reduced cupric salts very abundantly. Portion insoluble in water, dissolved in ether and alcohol.

A sample (20 grms.) of perfectly dry Waltham Abbey guncotton, representing the ordinary product of manufacture, was exposed in a bulb tube exhausted over mercury to 65° C. for seven hours daily. The mercury column was very gradually depressed, as in the preceding experiments with guncotton of this kind, and after the experiments had continued for ten weeks the gas escaped from the opening of the tube. In about one week more sufficient gas was collected for examination; it was found to consist of carbonic acid, 45.6 per cent.; nitric oxide, 10.8 per cent.; nitrogen, 43.5 per cent. Some water had become deposited on the sides of the tube, and a small quantity of mercury salt had formed. The application of heat to the tube was continued with the view of collecting a further quantity of gas, but the experiment was carried on uninterruptedly for a further period of nearly twelve months before a sufficient amount of gas (about 150 cc.) could be collected for analysis. This second product contained carbonic acid, 55.7 per cent.; hydrogen, 6.4 per cent.; hydrocarbons, traces; nitric oxide, 2.1 per cent.; nitrogen, 35.7 per cent. The total volume of gas evolved during fourteen months' exposure of the guncotton

to 65° C. for seven hours daily was about 660 cc. On removing the specimen from the bulb tube, it exhibited no alteration in colour, appearance, or explosiveness; the strength of fibre had slightly diminished; nitric acid was detected in small quantity in the aqueous extract, but no oxalic acid. A very slight reducing action was exerted upon cupric salts, but the proportion of matter soluble in ether and alcohol had not appreciably increased. At the conclusion of the experiment the specimen was washed in slightly alkaline water, dried, and exposed to strong daylight and occasional sunlight, in a stoppered bottle. Up to the present time (after nine months' exposure) the specimen has suffered no change whatever.

It would appear from these experiments, which were always commenced *in vacuo*, but continued after a short time in an atmosphere of the gaseous and volatile products formed, that guncotton, prepared and purified according to the system now in use, manifests some slight but undoubted symptoms of gradual change, if maintained for several hours at as low a temperature as 55° C. in a confined space; that a very long-continued exposure to that temperature does in some instances produce a notable alteration in the composition and explosive properties of the substance; that a similar change is somewhat more rapidly developed if the guncotton be exposed to temperatures of 60° C. and 65° C., but that the exposure of the substance several hours daily, even for months, to the highest of those temperatures does not so seriously affect the ordinary products of manufacture as to prevent their being afterwards restored, by the ordinary process of purification from acid, to a condition differing but little, practically, from that of the original material. Although these experiments were instituted with comparatively considerable quantities of guncotton (14-20 grms.), it must be at once admitted that, if the material were exposed in large compactly packed masses (5-10 kilos.) to the temperatures ranging between 55° C. and 65° C. for the periods given in the preceding experiments, it would be more seriously affected, and that the changes which would ultimately be developed by the free acid accumulating in the guncotton might give rise to spontaneous heating of the mass. On the other hand, it must be borne in mind that even the lowest of those temperatures occurs in nature only under exceptional circumstances, and for brief periods. It may, per-

haps, be considered that the arrangement of heating the guncotton over a column of mercury, adopted in the foregoing experiments, with the view of obtaining continuous records of the progress of change, was of a nature somewhat favourable to the material operated upon, because a small surface of mercury was exposed in direct contact with the gases or vapours evolved, and might, by its own oxidation, remove a portion of the generated acid which would otherwise have reacted injuriously upon the guncotton. It had indeed been stated, in the description of the experiments, that a few crystals of mercurous salt were always formed upon the exposed surface of the mercury, the production of the crystals being favoured by the condensation over the metal of a small quantity of water, produced as the experiment proceeded. But it must be borne in mind that the surface of mercury exposed was always very small (only from 78-100 sq. mm.) while the quantity of cotton operated upon was considerable, and that, between each consecutive period of exposure to heat, the guncotton absorbed, as it cooled during the night, the water impregnated with acid which had been previously expelled from it. Experimental proof was, however, obtained that ordinary guncotton, when exposed to 65° C. in vessels not closed by mercury, and so arranged that any liberated acid would not escape from contact with the material, was more rapidly and seriously affected than was the case in the globe experiments.

Four specimens, taken from different samples of guncotton, exposed in a dry state to 65° C. in very long and narrow-necked flasks seven hours daily for seven days, sustained no loss of weight. From the tenth to the fourteenth day, after the first exposure, all showed slight signs of decomposition, which proceeded with somewhat different rapidity in the several samples; two of them were completely decomposed in three weeks after the first exposure, the other two resisted for very considerably longer periods. Two other samples were similarly exposed to heat side by side; nitrous vapours became distinctly apparent six days after the first exposure to 65° C., and continued visible until the twelfth day's exposure. After three weeks' exposure the specimens had lost 30 per cent. in weight, and were converted chiefly into soluble guncotton. The protracted exposure of air-dry guncotton to a temperature ranging between 60° C. and 65° C. in a vessel *to which air had access* did not effect any

greater alteration in the material than was observed in the globe experiments. Thus some 50 grms. of air-dry guncotton, after exposure to heat seven hours daily for ten days, only lost 0·10 per cent. in weight. Two other specimens weighing 44 and 34 grms. were exposed day and night in a hot-air chamber to a temperature ranging between 35° C. and 50° C. The specimens were weighed periodically in an air-dry condition. After the lapse of ten weeks one sample had lost 1·18 per cent., and the other 1·56 per cent. In conducting these quantitative experiments, it was observed that the exposure of guncotton, for a protracted period, to a moderately elevated temperature, had the effect of reducing the hygroscopic power of the fibre, so that upon exposure of guncotton, which had been thus heated, to the atmosphere, the maximum proportion of moisture absorbed by it was very notably lower than that contained in the original sample. The actual loss sustained by the above samples, which were always weighed after exposure to air for definite periods, was therefore somewhat less than indicated by the numbers given.

CHAPTER XVII

ABEL ON PULPING GUNCOTTON AND THE EFFECT OF ALKALIS (1867)¹

Reduction of Guncotton Fibre to a Fine State of Division.—Abundant proofs have been obtained that the long-continued washing and the treatment with an alkaline liquid to which guncotton is submitted, do not completely separate from it products of the partial oxidation of organic impurities retained by the cotton up to the time of its conversion. This is unquestionably due in great measure to the tubular structure of the fibre. If the impurities were merely upon the surface of the fibre, their perfect removal by the action of solvents should be accomplished without difficulty, but it does not appear that even long-continued digestion of guncotton in alcohol has the effect of completely freeing it from the impurities soluble in that liquid. The action of alkalis upon the material might perhaps eventually result in the complete removal of these bodies, but the loss of product and destructive effect upon the fibre, resulting from any other than a brief digestion in a very dilute alkaline bath, are too considerable to admit of such a treatment.

The following experiments may be quoted in illustration of this. A quantity of guncotton which had already been submitted to the usual purification with water and a hot alkaline bath, was boiled for ten minutes in a solution of potassium carbonate of the strength usually employed (sp. gr. 1.02). By this treatment the material sustained a loss of 3.7 per cent., the bath having assumed an amber colour. Upon being again boiled for twenty minutes in the same alkaline bath, which thereby became considerably deepened in colour, the sample sustained a further loss of 12.09 per cent. The strength of the fibre had been considerably reduced by this treatment. Guncotton to the amount of 6.5 grms. and 0.4 grm. of sodium carbonate were placed together with 50 cc. of water in a flask to which a vertical condenser was attached, and were heated to

¹ *Trans. Roy. Soc.* (1867), 181-253.

100° C. for twelve hours. The alkali was then found to have become nearly neutralized, and the dark brown liquid contained sodium nitrate in abundance. The guncotton was washed and twice treated in the same manner, the alkali being neutralized on each occasion, as in the first instance. But though it is evident that the treatment of guncotton with warm alkaline baths cannot be advantageously extended, satisfactory proof has been obtained that the stability of guncotton which has been purified as far as is possible by the present system, may be importantly increased by submitting the material to a special process of washing.

In the experiments instituted upon the application of guncotton as a substitute for gunpowder, some very advantageous results have attended the conversion of the material into homogeneous masses of any desirable form or density, by preparing it according to the method commonly employed for converting rags into paper. In reducing the material to a very fine state of division by means of the ordinary beating and pulping machines, the capillary power of the fibre is nearly destroyed, and the guncotton is, for a considerable period, very violently agitated in a large volume of water. It would be very difficult to devise a more perfect cleansing process than that to which the guncotton is submitted; and the natural result of its application is that the material thus additionally purified acquires considerably increased powers of resisting the destructive effects of heat. Samples of the pulped guncotton, even in the most porous conditions, have been found to resist change perfectly upon long-continued exposure to temperatures which developed marked symptoms of decomposition in the guncotton purified only as usual. The pulping process applied to guncotton affords, therefore, important additional means of purifying the material, the value of which may be further enhanced by employing a slightly alkaline water in the pulping machine. The slightest change sustained by guncotton is attended by the development of free acid, which, if it accumulates in the material, even to a very trifling extent, greatly promotes decomposition.

Numerous experimental data have been collected with respect to the establishment and acceleration of decomposition in guncotton by free acid whilst exposed to light or elevated temperature. This acid is present either in the imperfectly

purified material or has been developed by decomposition of guncotton or its organic impurities. Samples of guncotton which, by exposure to elevated temperatures or for considerable periods to strong daylight, had sustained changes resulting in a considerable development of acid, have afterwards been thoroughly purified by washing. When exposed to light for months, and in some instances for two or three years (up to the present time), they have undergone no further change, while corresponding samples confined in close vessels without being purified, have continued, in some instances, to undergo decomposition, and the original substance has been completely transformed into the products repeatedly spoken of. Instances have, however, occurred in these experiments (and have already been quoted) in which guncotton has resisted further change, even under these circumstances. Guncotton purified as usual has been confined in stoppered glass bottles, having previously been rendered slightly acid with nitric acid. In these instances the guncotton has always undergone decomposition upon exposure to light, the rapidity of its change varying with the quality of the material. Two specimens of Waltham Abbey guncotton (coarse and fine yarn) were introduced into well-stoppered bottles, and nitrogen peroxide was then passed into them for a short time. The bottles were then tightly closed and placed in a dark cupboard, being inspected from time to time. The gas was rapidly absorbed by the guncotton, which assumed a green tinge and gradually contracted, the colour of the vapours in the bottles slowly becoming deeper again. After the lapse of two months both samples had contracted into compact masses, occupying less than one-fourth the original volume. Both were coloured green, and dark orange vapours filled the vessels. From this period the nitrogen peroxide diminished in quantity very gradually until, about eighteen months after commencing the experiment, the atmosphere in the bottles was perfectly colourless. The coarse guncotton had passed into a viscid mass, exhibiting the usual characters; the fine guncotton, though it contracted to about one-tenth of its original volume, still retained to some extent its original appearance. Crystals of oxalic acid were dispersed through the mass. Two other samples of guncotton, from the preceding experiment, were placed in bottles into which nitrous acid, produced by means of starch, was passed. These bottles were afterwards also

placed in the dark. The gas was gradually absorbed by the guncotton, the atmosphere in the bottles became colourless, and both samples were highly bleached. After the lapse of two months, a faint orange colour was exhibited, but the specimens of guncotton had undergone no apparent change whatever. Three months later, the bottle containing the coarse yarn exhibited deep orange vapours, the guncotton had contracted somewhat and assumed a green tinge. The other sample exhibited no signs of change, but a faint orange tinge which did not increase afterwards was manifest in the bottle. Twenty-eight months after the commencement of the experiment this sample exhibits no signs of change beyond a very slight contraction. The coarse yarn has contracted to about one-third its original volume, is friable, and partly soluble in water. Nitrogen peroxide, if left in contact with guncotton, is therefore much more rapid in its destructive action than nitrous acid; guncotton when confined together with either of them undergoes gradual decomposition even in the dark.

A sample of guncotton which had been found to decompose very readily at 100° C., was placed in a retort suitably fitted with a delivery tube, and the gases disengaged from it were passed into four bottles containing different samples of guncotton. These were then perfectly closed and exposed to strong daylight. The first sample soon began to exhibit signs of change. The colour of the vapours increased in depth, and in one month's time had become very deep coloured, the guncotton having assumed a greenish tinge from absorption of gas. The sample was then placed in the dark, after which it underwent further change very gradually, first contracting considerably, and afterwards, after the lapse of upwards of one year, becoming a somewhat hard gum-like mass. In the case of the second and third samples, the coloured vapours disappeared at first almost entirely, but the atmosphere in the bottles became coloured again after one month's exposure to light. The depth of colour increased so rapidly in one instance that two months after the first exposure to light the bottle was placed in the dark. The change in the two bottles then proceeded at about the same rate. The specimens contracted very slowly, and the nitrous vapours disappeared gradually. At present, $2\frac{1}{4}$ years after commencement of the experiment, the specimen which has been exposed to

light is scarcely as much changed as the one which after a time was placed in the dark; both have contracted to about one-half their original volumes, but have preserved their normal appearance; a few very minute crystals (probably oxalic acid) are perceptible upon the sides of the bottle which has been kept in the dark.

The fourth sample (prepared at Waltham Abbey in 1863) has resisted change to a remarkable extent. The vapours were at first entirely absorbed, and the guncotton has become slightly bleached. A faint orange tint was first observable in the bottle after it had been exposed to strong daylight for six months. Nitrous vapours were then slowly evolved until the depth of colour was somewhat considerable. After the lapse of several months they gradually diminished again, and ultimately disappeared once more, after about eighteen months' exposure. After the lapse of $2\frac{1}{4}$ years the guncotton has contracted only slightly, but exhibits no other signs of change. There can be no doubt, however, judging from this contraction and from the evolution of vapours at one period of exposure, that this sample has suffered change which would not have occurred had it been exposed to light under ordinary conditions.

The experiments in sealed tubes which have been described—the results of examination of gases collected from guncotton which has been exposed to heat for long periods in contact with them—and the general existence of nitric acid in samples of decomposed guncotton, appear to show that the first effect of exposure of the ordinary material to sufficient heat is the disengagement of nitrogen peroxide and the production of water, by which the former is converted into the nitric and nitrous acids. The latter, if allowed to remain in contact with the heated guncotton, is gradually reduced to nitric oxide, and finally the nitrogen becomes deoxidized at the expense of the hydrogen and carbon—oxalic and carbonic acids being eventually furnished by the latter. The nitric acid produced attacks the guncotton at the same time; the presence of very small quantities of this substance in guncotton greatly accelerates the decomposition of the material by heat. One drop of concentrated nitric acid introduced into vessels containing 2 or 3 grms. of guncotton invariably brought about rapid decomposition at comparatively low temperatures (55° C. to 65° C.); and by operating at temperatures between 70° C. and 100° C. with small

samples of guncotton to which as small a quantity as possible of dilute nitric acid was added, they were in this way gradually converted into the gum-like product in a few hours, though instances occurred occasionally in which, even under these severe conditions, the material resisted decomposition to a remarkable extent.

In many experiments instituted with ordinary guncotton at 90° C. and 100° C. it was found that, if the mode of operating were such as to facilitate the escape from the apparatus of any acid vapours evolved, the guncotton would frequently resist decomposition in a remarkable manner, being only very gradually converted into the final products. The two following experiments demonstrate how greatly decomposition at 100° C. can be retarded by impeding the destructive action of acid generated by the exposure to a high temperature. Weighed quantities (about 1.5 grms.) of dry guncotton were loosely packed into two narrow U-tubes, which were immersed in a water-bath and connected with an aspirator. The guncotton was in both instances maintained during the day at 100° C. A moderately rapid current of air was passed through one tube, and air was allowed to circulate very slowly through the other. At night both tubes were closed up with corks. The weight was determined at intervals. The following were the results obtained:—

Hours of Heating.	Percentage Loss.	
	Slow Current.	Rapid Current.
24 . . .	17.47	4.8
64 . . .	50.93	8.92
260	13.96

The results of these and the preceding experiments warrant the conclusion, that as soon as acid becomes liberated in guncotton, changes are developed in the material which would not be brought about by its simple exposure to heat, provided no free acid were present in it. If, therefore, it be possible to neutralize, at the instant of its liberation, any acid which may be produced by the effect of elevated temperatures upon the comparatively unstable impurities contained in small quantities in guncotton, the latter might be expected to resist alteration under circumstances which, if the first acidity were not counteracted, must determine the decomposition of the material.

CHAPTER XVIII

ABEL ON THE EFFECT OF ALKALIS ON GUNCOTTON (1867)¹

REFERENCE has been made, on more than one occasion, to the influence which certain mineral impurities of general occurrence in guncotton (earthy carbonates) were observed to exert upon the rapidity with which the substance sustained alteration upon exposure to heat. Some samples which were heated for comparatively considerable periods without exhibiting signs of change were found to contain much larger proportions of calcium and magnesium carbonates than specimens with which, in other respects, they were identical. This observation led, at an early stage of these investigations, to careful observations of the comparative effects of high temperatures (100° C. and 90° C.) upon a variety of samples which were known to vary as regards the proportions of earthy and alkaline carbonates distributed through them. Some specimens were repeatedly rinsed in distilled water (whereby the larger proportion of earthy carbonates attached to the fibre was removed) and exposed to heat, in comparison with corresponding specimens not thus treated. Some other samples were extracted with dilute acid and washed; but as acetic acid was used in most experiments, the results of their exposure to heat were not of the nature anticipated, for the reason, as already explained, that the treatment in question removed not merely carbonates but also a proportion of the organic impurities. The extraction of guncotton with dilute hydrochloric acid does not remove organic impurities; and as has already been shown, this treatment has the effect of rendering ordinary guncotton more susceptible to the destructive effects of high temperatures.

A considerable quantity of Waltham Abbey guncotton, after having been purified in the usual way, was saturated with a solution of sodium carbonate of sufficient strength to deposit from 0.4 to 0.5 per cent. of the salt in the guncotton, after the latter had been expressed in the hydro-

¹ *Trans. Roy. Soc.* (1867), 181-253.

extractor and dried. Portions of the material thus prepared were carefully washed out in distilled water, and submitted to heat in comparison with corresponding samples of the "alkalized" guncotton. The washing process did not merely extract the sodium carbonate, it also effected the mechanical removal of a large proportion of the earthy carbonates deposited upon the guncotton during the long-continued washing in spring or river water. Experiments carried out at 100° C. showed that whilst with "alkalized" guncotton seven or eight hours elapsed before any symptom of decomposition was observed, with ordinary guncotton decomposition became manifest in two and four hours. When once guncotton begins to undergo considerable change, decomposition proceeds more rapidly in untreated material than in the "alkalized" samples. The protective power exerted by small proportions of carbonates was shown when it was observed that an "alkalized" sample exhibited no signs of change until after the lapse of seven hours, whilst equal quantities of the same sample, purified from carbonates by washing, exploded after exposure to 100° C. for 1½ hours. The small proportion of earthy carbonates ordinarily existing in guncotton exerts a decided protective action. Experiments also afforded a very decided proof that the silicating process prescribed by von Lenk exerts some amount of protective influence upon the guncotton when exposed to heat, though this result is not due, as supposed by him, to the closing up of the fibre by an insoluble silicate, but simply to the deposition of a small quantity of earthy (and possibly of alkaline) carbonate upon the fibre, when the silicate undergoes decomposition during the drying and the subsequent washing process. The amount of protection thus afforded to the guncotton is, however, obviously as liable to variation as that resulting from the deposition of calcium and magnesium carbonates upon the material during the long-continued immersion in flowing water. Numerous specimens of cotton which had been silicated, varied greatly in their powers of resisting change at high temperatures, but they were invariably rendered decidedly more prone to change if thoroughly washed in distilled water previous to their exposure to heat.

It is remarkable how very small a proportion of a carbonate, deposited upon the fibre of guncotton, exerts a notable influence upon its power of resisting the effects of heat. Thus, a portion

of a sample of guncotton which had been carefully freed from carbonates, was saturated with perfectly clear lime-water, wrung out and dried. Upon exposure to 100°C . in comparison with an equal weight of the sample purified from carbonates, the very small quantity of calcium carbonate which had been deposited upon the guncotton proved sufficient to delay, to a notable extent, the period of first decomposition, and to modify somewhat the results of change produced by exposure for a definite period at 100°C . In an experiment conducted at 90°C ., the "alkalized" guncotton was heated in a flask to which a delivery tube was attached, and the gas which escaped was examined. It was then observed that, upon the second day's exposure, a very small quantity of carbonic acid was continuously evolved; that the quantity increased somewhat upon the third day; and that no nitrous vapours escaped until the sixth day, when the temperature was accidentally raised to 95°C . Carbonic acid was then still evolved in small quantity. Similar evidence of the slow decomposition of the carbonate, which always preceded any disengagement of nitrous acid, was obtained in other experiments. Some experiments were instituted in *sealed tubes* with the guncotton impregnated with 0.4 per cent. of sodium carbonate. A specimen was enclosed in a tube with air at the atmospheric pressure, and exposed to 100°C . for $3\frac{3}{4}$ hours, on the first day, during which period no trace of nitrous vapour was visible. It was afterwards heated to 100°C . six hours daily for thirteen days, and no coloration of the air in the tube was observed at any time during this treatment. After four days' exposure the tube was opened and gas escaped under somewhat considerable pressure. The tube was sealed up again, and at the close of the experiment it was opened once more, when gas escaped only under slight pressure. The specimen became discoloured in a few places after some time (which is invariably the case when guncotton containing alkaline matter is exposed to a high temperature), but exhibited no other signs of change. In similar experiments conducted with ordinary guncotton, deep nitrous vapours were observed in the tubes within three hours from the commencement of the experiment, and the material was always converted into a gum-like mass; in some instances the tube exploded violently after a time.

An experiment similar to the preceding was instituted with "alkalized" guncotton in a more closely packed condition, the

tube being exhausted, filled with nitrogen, and re-exhausted before sealing. This tube was heated to 100° C. for ten hours (in two days), and afterwards left exposed to light for twenty-four hours, without the slightest coloration by nitrous vapours being observed. On being again heated, very faint nitrous vapours were observed after two hours' exposure; these did not increase at all, but disappeared entirely after continuation of the heating for four hours longer. When the tube had been heated for six days the point was opened and gas escaped under considerable pressure. The tube was again closed and heated for nine days, six hours daily; upon afterwards opening it, gas escaped only under slight pressure. It was again heated to 100° C. for seven days, when the tube was accidentally fractured by the effects of a neighbouring explosion. At this time the guncotton had become darkened in some places and had an acid reaction, but exhibited little other signs of change. Several experiments were conducted with guncotton containing considerably larger proportions of sodium carbonate than the samples previously employed, for the purpose of obtaining data with regard to the progressive changes resulting from the protracted exposure of "alkalized" guncotton to heat. The results obtained are fairly represented by the following selected experiments.

Six and a half grms. of Waltham Abbey guncotton were impregnated with 0.45 gm. of sodium carbonate. The air-dry specimen was exposed to 100° C. (for five or six hours daily), loosely packed in a narrow-necked flask. Small weighed quantities of the sample (from 0.07 to 0.1 gm.) were removed from the flask for examination each morning before heat was again applied. The darkening, always produced by heating guncotton with an alkaline substance, commenced upon the first day's exposure to heat, but no other effect was noticed; after six days' exposure the guncotton was still slightly alkaline, the coloration having gradually increased, until some parts exhibited a brown tint. In other respects the substance was unchanged. After the ninth day's heating the guncotton was found to be quite neutral. About one-fifth of the specimen was then removed for examination. Water extracted the colouring matter entirely, and a brown solution was obtained, in which sodium nitrite were readily detected. The liquid also reduced cupric salts slightly. The guncotton itself had not suffered any

change in explosiveness or strength of fibre, nor had the solubility in ether and alcohol increased appreciably. The exposure of the sample to 100° C. was continued for seven days longer. On the sixth day a small portion was examined and found to be still neutral. On the seventh day the atmosphere in the flask was found to have an acid reaction, though no nitrous vapours were perceptible. Upon determining the weight of the guncotton (after deducting the portions used during the experiment), it was found by calculation that the loss which it had sustained during exposure to heat for 100 hours (in sixteen days) was greater than would have been caused by the complete expulsion of carbonic acid from the carbonate employed. The aqueous extract was highly coloured, the guncotton being left almost colourless. Sodium nitrate and nitrite existed plentifully in the liquid, and the latter reduced cupric oxide in an alkaline solution. The washed guncotton was found, as might have been anticipated, to have sustained a greater loss than would have been caused by the extraction of the alkaline base entirely in the form of nitrate. The guncotton soluble in ether and alcohol, now contained in the specimen, amounted to 6.98 per cent.; the material originally contained 2.3 per cent.; the increase amounted, therefore, only to 4.68 per cent. The proportion of nitrogen oxides which would have been liberated by the reduction to that extent of trinitrocellulose even to the lowest of the substitution products would not have sufficed to decompose the sodium carbonate present. It would appear from these results that the principal effect of the very long-continued exposure of this "alkalized" guncotton was to establish a very gradual action of the alkaline carbonate upon the guncotton (resulting in the production of glucic acid, etc.), and that even the *first* stage of decomposition (consisting in the reduction to soluble guncotton) caused simply by the action of heat upon the ordinary material, only proceeded to a very slight extent during the sixteen days' treatment. 6.5 grms. of guncotton were impregnated with 0.38 grm. of sodium carbonate. The sample was thoroughly dried and exposed to 100° C. as in the preceding experiment. After the lapse of three days a weighed sample of the guncotton was examined. It had darkened somewhat, was alkaline and exhibited no change of properties. After six days' exposure it was still alkaline, and its solubility in ether and alcohol had not increased appreciably.

Upon the ninth day the sample was found to be neutral. The experiment was then stopped, the guncotton was extracted with water, and the proportion of nitrogen acids existing in it as sodium salts was determined by means of nascent hydrogen. The result showed that less than four-tenths of the sodium carbonate employed had been neutralized by those acids, the remainder existing in combination with organic acids. Traces of ammonia were evolved during the treatment of the guncotton in this and the preceding experiment, and the loss in weight sustained by the material was greater than would have been occasioned by the simple expulsion of carbonic acid from the carbonate. The solubility in ether and alcohol of the sample had only increased to about double the original proportion. It was of course impossible to demonstrate by experiment whether the small proportion of organic acid produced in these experiments was glucic acid.

When guncotton is impregnated with about 5 per cent. of sodium carbonate and heated at 100° C. for six days, it becomes considerably darker, and, of the sodium salts present, due to decomposition of the guncotton, only some 20 per cent. consists of sodium nitrate and nitrite, the rest consisting of organic salts of sodium. It was not possible to determine whether the small proportion of organic acid produced by decomposition was glucic acid, resulting from the action of the alkali upon the guncotton, or whether it consisted of the pectic acids found in the products of spontaneous decomposition; but as abundant proof exists that the latter are only the products of a *secondary* change resulting from the action upon guncotton of liberated nitrogen acids, there appear to be very good grounds for the conclusion that the results obtained in these experiments were mainly ascribable to the action of the alkaline carbonate upon the guncotton and the organic impurities present, and that the effects exclusively due to the protracted exposure of the substance to 100° C. were limited to the liberation of a very small proportion of nitrogen acid, which was at once neutralized, the only change produced in the guncotton consisting, therefore, in the decomposition of the small quantities of comparatively unstable organic impurities, and in a slight increase of the proportion of soluble guncotton.

The power possessed by carbonates to prevent or arrest the decomposition of guncotton when exposed to high tem-

peratures has been demonstrated in a striking manner by some experiments which have, at the same time, furnished evidence in support of the conclusion that the organic impurities contained in guncotton constitute the primary cause of its susceptibility to change under the influence of heat and light. Specimens of guncotton were exposed in flasks to 90° C. and 100° C. until decomposition was established to such an extent that the vessels were filled with deep-coloured vapours; a small quantity of calcium or magnesium carbonate was then introduced into the flask, or the guncotton was removed from the vessel, dusted over with a carbonate, and immediately replaced. Decomposition was at once arrested by these means; moreover, the guncotton no longer exhibited any susceptibility to decompose even if exposed to 90° C. and 100° C. for several successive days. About 5 grms. of ordinary guncotton were dusted over with finely pulverized potassium bicarbonate and exposed to about 95° C. in a long-necked flask side by side with a corresponding quantity of the same specimen of guncotton in its ordinary condition. The "alkalized" guncotton gradually darkened upon the second day's exposure, eventually assuming a brown colour. After exposure to the above temperature during five days for seven hours daily, the unprepared guncotton began to evolve nitrous vapours abundantly. The examination of a small specimen showed that the sample had undergone very little change, the solubility in ether and alcohol having slightly increased. It was now removed from the flask, dusted over with powdered carbonate, and immediately re-exposed to heat. All decomposition ceased, the guncotton behaving exactly like the specimen which was originally alkalinized, except that the usual darkening took place very slowly indeed. When it had been maintained at 95°-100° C. seven hours daily for eight days, it was still alkaline; after treatment with water, it exhibited all the original properties of the guncotton; the solubility in ether and alcohol had undergone no increase since the alkaline salt was applied. The other specimen to which the carbonate had been applied in the first instance was examined after exposure to 95° C. for seven days. The aqueous extract had a brownish colour, and reduced cupric salts to a very slight extent. The extracted guncotton was perfectly white; the strength of fibre, explosiveness, and solubility in ether and alcohol had undergone no change. It

was now dried and again exposed in a clean flask to 95°-100° C. During six days it had not exhibited the slightest indication of decomposition, no acidity has yet been developed in it, and it is still unchanged in all its properties. It would appear from these experiments that a carbonate applied in the most simple manner to guncotton in which decomposition has been established will effectually arrest the change; and that if guncotton containing a carbonate be exposed for some time to heat, the latter promotes the transformation of the unstable organic impurities into products fixed by the base, the result being that guncotton undergoes a searching purification from these substances, and afterwards exhibits, in consequence, a remarkable stability under very severe conditions of exposure to heat.

A number of experiments have been instituted on the comparative effect of exposure to 90° C. and 60° C. of samples of guncotton impregnated with different proportions of alkaline carbonates ranging from 1 to 10 per cent., the object being to ascertain whether the first-named proportion would suffice to afford security against the development of free acid in the guncotton even under conditions of exposure to heat much more severe than could ever be met with in natural practice, or to determine what proportion might be necessary for that purpose. The results of these experiments showed that 1 per cent. of sodium carbonate, uniformly distributed through guncotton, produced but very little darkening effect upon the material, even when the latter was exposed seven hours daily for several weeks (three weeks and upwards) to 95° C. or 100° C., and that no free acid was developed by a continuation of exposure to 95°-100° C. for three weeks. Guncotton containing 4 per cent. of the carbonate did not change colour to a much greater extent, and exhibited still a distinct alkaline reaction after exposure to 95°-100° C. for four weeks. Samples containing from 4 per cent. upwards of alkaline carbonate darkened very considerably upon a long-continued exposure to heat; and a trifling loss in weight was sustained by them, in instances when the treatment was continued between four and five months. This loss somewhat exceeded that which would have been simply occasioned by expulsion of the entire carbonic acid contained in the sodium salts, and furnished evidence of the escape of small proportions of volatile matter. The strength of the fibre was not appreciably affected even in the experiments continued

for a considerable period at 90°-100° C. with the samples containing the highest proportions of carbonates. The colouring matter produced by the action of the alkali was entirely extracted by water; and the properties of the guncotton were unchanged. It therefore appears that, although the presence of somewhat considerable proportions of alkaline carbonate (even as much as 10 per cent.) in guncotton does not exert any important action which can be pronounced prejudicial even under very severe conditions of exposure to heat, a proportion as low as 1 per cent. suffices to protect the material, for a longer period than ever could occur in actual practice, from the destructive action of such acid as may be liberated by decomposition of the organic impurities, or by the very gradual effect of a high temperature (90°-100° C.) upon the pure guncotton. The introduction of considerable quantities of saline matter into guncotton necessarily gives rise to the production of smoke and to some deposition of solid residue, upon explosion of the substance, and although the amount of both these products would then still be very trifling as compared with those of a corresponding character resulting from the explosion of gunpowder, it is inadvisable that they should be unnecessarily increased. It therefore appears preferable to limit the extent of impregnation of guncotton with sodium carbonate to 1 per cent. It has been abundantly demonstrated by the experiments detailed, and by one instituted upon a more considerable scale, to be presently described, that even the introduction of one half that proportion of sodium carbonate into guncotton serves to afford it sufficient protection under conditions of exposure to heat exceeding in severity and duration any which the material would have to encounter if substituted for gunpowder in all directions.

CHAPTER XIX

ABEL ON THE PROTECTIVE ACTION OF WATER ON GUNCOTTON (1867)¹

IN one of the earlier experiments on the effects of exposure of guncotton to 100° C., it was found that the accidental introduction of a very small quantity of water into the vessel containing the guncotton, afforded most perfect protection to the material, which exhibited no signs of change during sixteen hours' exposure to 100° C., and had not sustained any loss in weight at the close of the experiment. This power possessed by water (or aqueous vapour) of preserving guncotton from decomposition at high temperatures is remarkably at variance with the influence exerted by moisture, if confined together with guncotton under protracted exposure to bright daylight and sunlight, in which case there appears no doubt, from the results which have been described, that the aqueous vapour operates in determining to a slight extent the decomposition of the material. Further illustrations, though less striking than the one above quoted, were furnished of the protective effect of aqueous vapour, by the comparative tardiness with which certain samples of guncotton containing more than the ordinary proportion of hygroscopic moisture underwent change by exposure to high temperatures. This preservative power of water has received the fullest demonstration from the results of a considerable number of experiments, the nature of which is fairly represented by the following examples. A hank of guncotton was suspended in the upper part of a capacious flask containing distilled water tinted with litmus. The water was maintained in rapid ebullition for several hours, the greater portion of the steam condensed in the neck of the flask and upon the guncotton returning to the body of the water. At the conclusion of the experiment the tint of the litmus (compared with a standard) had not been affected in the slightest, and the guncotton was perfectly neutral and unaltered. A long wide

¹ *Trans. Roy. Soc.* (1867), 181-253.

glass tube was loosely filled with guncotton. One extremity was drawn out to a beak which was immersed in water tinted with litmus, the other end was connected with a small boiler from which a rapid current of steam was passed over the guncotton, uninterruptedly, seven hours daily for three days. Not the slightest alteration was produced in the colour of the litmus, and the guncotton was unchanged. A stout glass tube, closed at one end, was partly filled with guncotton; sufficient water was introduced to cover the latter, and the tube was then sealed and exposed to 100° C. seven hours daily for six days. When the tube was opened no gas escaped, the water was not acid, and the guncotton exhibited no signs of alteration. The open tube was afterwards exposed to strong daylight and sunlight; after the lapse of eight months the guncotton was found to have a very faint acid reaction, and a minute trace of nitric acid was detected in the water. The proportion of matter soluble in ether and alcohol had very slightly increased. Some guncotton was saturated with water, which was afterwards expressed to such an extent that the specimen was difficultly combustible when held in a flame. In this condition the sample was exposed in a sealed tube at 100° C. seven hours daily for twenty-four days. When the tube was opened no gas issued from it; the guncotton exhibited a very faint acid reaction, but no other signs of change. The open tube containing the moist specimen was afterwards exposed to strong daylight and sunlight for six months; the guncotton was then found to have a decided acid reaction. It was digested with a small quantity of water: the aqueous extract was acid to test paper but not to taste; nitric acid was detected in it, but no oxalic acid; potassium hydroxide imparted to it a faintish yellow tinge, and the alkaline liquid reduced cupric salts to a slight extent. The proportion of matter extracted by ether and alcohol was about double the amount originally existing in the sample. The strength of the fibre was unaltered, and there was no appreciable diminution of the explosiveness of the guncotton. Seven grms. of guncotton were thoroughly moistened by being suspended for some time in an atmosphere of steam; the sample was then placed in a flask the sides of which were previously moistened. This flask was connected by a delivery tube with another containing water, and was also fitted with a straight narrow glass tube. A small quantity of steam was passed into the flask from time to time

as the moisture became partially expelled during the experiment. After three days' exposure to 100° C. (six hours daily) a weighed sample was removed for examination. The guncotton had become slightly discoloured in a few places, where it was in immediate contact with the sides of the flask. Water extracted a minute quantity of colouring matter; no other effect of the exposure to heat was observed. The guncotton was again heated to 100° C. for five days (six hours daily); it was then removed, the flask dried and weighed. By these eight days' exposure to 100° C., in a moist atmosphere, it had sustained a loss of only 1.7 per cent. A weighed sample was again examined; it furnished a very faint indication of acidity. The reactions of nitric acid could not be obtained with the aqueous extract; the proportion of matter extractable by ether and alcohol had very slightly increased. The sample was again moistened, and exposed to 100° C., as before, for nine days; at the expiration of this period it had sustained a further loss of 1.01 per cent. The total loss during the seventeen days' treatment amounted, therefore, to 2.71 per cent. The condition of the sample was now as follows:—It had darkened in a few places where in close contact with the glass, and possessed a faint odour, such as is always observed in guncotton which has been stored for some time in a warm locality; its acidity had not increased, but a faint reaction of nitric acid was obtained in the aqueous extract, after concentration to a small bulk. A trace of lime was also found in solution (evidently as calcium nitrate produced from carbonate in the sample). The proportion of matter extracted by ether and alcohol amounted to 4.1 per cent.; in its original condition the sample contained 2.3 per cent.

Six and a half grms. of guncotton were saturated with moisture and placed in a flask fitted with a straight narrow glass tube of considerable length, for the purpose of rendering the expulsion of water very gradual. After exposure to 100° C. six hours daily for three days the specimen was still moist. The examination of a weighed sample did not furnish the slightest indications of change. The same negative result attended the examination of a second sample after further exposure of the guncotton to 100° C. for three days. The apparatus now contained but very little moisture; after a renewed exposure for three hours to 100° C., a very faint coloration by nitrous vapours was observed in the flask; a

sample was examined, but beyond a faint acidity no signs of change were detected. The heat was continued for four hours more on the same day, at the expiration of which the coloration in the flask was somewhat more distinct; but there were no signs of nitrous vapour on the following morning. The indication of change in the guncotton was still limited to a very faint acidity. The sample was once more heated for six hours, during which period no trace of moisture was deposited upon the cool portions of the glass. Nitrous vapours appeared again in very small quantity, and did not increase up to the termination of the experiment; but on the following morning the apparatus contained deep-coloured vapours. The guncotton was now extracted with water; the liquid contained a small quantity of nitric acid, but did not reduce cupric salts. The washed guncotton was almost perfectly soluble in ether and alcohol; the insoluble portion amounted only to 1.25 per cent.

Six and a half grms. of guncotton, in an air-dry condition, were placed in a capacious flask (the interior surface of which had been previously moistened) fitted with a long narrow glass tube. A piece of litmus was suspended in the neck of the flask. Shortly after the guncotton had been first exposed to 100° C. the litmus gradually assumed a wine-red tint, and when the heating had been continued for five hours, the paper had become bleached. There was no other indication of further change. At the expiration of the second day's heating, the small quantity of water which had condensed in the neck of the flask exhibited an acid reaction, and the guncotton possessed the peculiar odour which has repeatedly been referred to. Towards the close of the third day no trace of moisture was visible in the cool portion of the flask; a very small quantity was deposited some distance up the quill-tube. Soon afterwards a faint coloration by nitrous vapours was observed, which had very considerably increased by the following morning. The guncotton was then found to be acid, the strength of fibre and explosiveness had both diminished; the aqueous extract contained nitric acid, but not oxalic acid, nor did it reduce cupric salts even when highly concentrated. About three-fourths of the washed guncotton dissolved in ether and alcohol, a portion being rapidly dissolved, the remainder more slowly; the more soluble part yielded a tough collodion film.

The following points of interest and importance are estab-

lished by the results of these and other similar experiments:—

(1) Guncotton immersed in water perfectly resists decomposition when exposed for long-continued periods to 100° C.; and this severe treatment has no effect upon the material, even if it is only in a moist condition, or confined in an atmosphere of aqueous vapour. But if the moist specimens are exposed to bright daylight and sunlight for a considerable period, the water or aqueous vapour does not exert the same protective power. (2) If the water or aqueous vapour is allowed to escape during exposure to 100° C. until the guncotton and the atmosphere surrounding it have become almost dry, decomposition commences very gradually; and by arresting the change at a particular period the material is found to be completely reduced to soluble guncotton, without the formation of any appreciable amount of the secondary products which result from the action of liberated acid upon the cellulose products. The perfect protection afforded by moisture to guncotton at 100° C., under severe conditions, rendered any experiments in this direction at somewhat lower temperatures unnecessary.

The following experiment furnishes, however, interesting confirmation of the results obtained by operating at higher temperatures. 69·706 grms. of guncotton in an air-dry condition, and 52·196 grms. of the same sample soaked in distilled water, which was afterwards expressed as completely as possible, were introduced into large bottles, into which the stoppers were loosely inserted. These were then placed in a water-oven, the temperature of which was maintained continually at 60°-65° C. day and night. At the expiration of two months both samples were weighed in an air-dry condition. The results indicated a loss of weight of 12·8 per cent. in the dry sample, and of only 0·13 per cent. in the other. After further exposure of the samples as before, for five weeks, the vessel containing the dry one was filled with very deep-coloured vapours, and the experiment was therefore interrupted and the samples were again weighed. The dry specimen had sustained a loss of 34 per cent., was quite friable, and had become converted partly into soluble guncotton and partly into the products soluble in water. The sample which had been exposed in a moist condition had sustained a total loss of 0·89 per cent., and did not exhibit the slightest signs of acidity. This sample was again submitted, in a moist state, to a warm

atmosphere, ranging from 55° to 65° C., day and night for four calendar months. The total loss which it had then sustained after continuous exposure to heat for between seven and eight months amounted to 1.47 per cent. The guncotton exhibited no acid reaction, and the moisture condensed upon the sides of the bottle gave only a faint indication with litmus paper.

Careful observations have been instituted upon the storage of considerable quantities of the material in a wet or merely moist condition. Ordinary guncotton has been immersed in sufficient distilled water just to cover it, and has been kept in that condition in closed vessels, with light excluded, for 2½ years. It is perhaps scarcely necessary to state that the material has not sustained the slightest change, and that the distilled water in which it has been preserved is perfectly neutral, the only impurity found in the latter being a small quantity of saline matter extracted from the guncotton. A portion of this sample was transferred to a large glass bottle twelve months ago, and has been left exposed to diffused daylight. This difference in the mode of preservation has been quite without effect upon the guncotton.

The principal stock of guncotton manufactured at Waltham Abbey for experimental purposes, amounting to about 3000 lb., has been preserved in a moist condition (just as obtained from the centrifugal hydro-extractor) in closed cases until required for use, some of the packages having been kept for about two years; a few, specially set apart for periodical examination, have been preserved for about three years. I have to record no indications of the slightest change except in instances where the guncotton had been preserved in close contact with the tinned copper linings of some gunpowder cases used for its storage. It was found, after some time, that the surfaces of these became oxidized where they were in contact with the moist material, and that this oxidation determined the development of an acid reaction in the guncotton, which, however, was, and has continued to be, confined to the portions in immediate contact with the surface of the metal. Guncotton in the condition above referred to contains sufficient water to render it quite unflammable. It may therefore be preserved with perfect safety in this convenient condition, and may be at any time prepared for use by desiccation. As far as can be concluded from three years' experience, the close packing of guncotton in this damp

state is not even in the slightest degree injurious to the structure of the fibre; no tendency whatever of the material to become rotten when thus preserved has yet been discovered. On the contrary, most decided evidence has been obtained that guncotton, when kept in a damp condition, is very considerably more permanent than ordinary cotton, or vegetable substances of a similar nature. Thus, many hanks of the guncotton stored in the damp state were tied with tape and string for purposes of distinction. Upon examining these hanks ten months after they had been packed, the tape was in all instances found to be almost, if not entirely, destroyed, crumbling away when touched, and being transformed principally into fungoid bodies; the strings were also quite rotten and covered with vegetable growth, but the guncotton even in close proximity to them was unaffected. Similar results were observed in the case of a number of samples of guncotton which had been packed in a dry condition in paper envelopes and placed in a small very damp chamber. About twelve months after they were stored the paper wrappings and string were found to be covered with vegetable growth and partly destroyed, while no vestiges of similar growth, or other signs of change, were detected in the guncotton. A wooden reel, having some guncotton yarn wound upon it, which had been kept in the same locality, was also found to be covered in all exposed parts with fungoid growth, but the guncotton, in immediate contact with the latter upon the wood, was unaffected and perfectly free from mildew. This specimen has been preserved for another year in a damp atmosphere upon the reel and exposed to light. In some parts the mildew has extended to the guncotton immediately in contact with the wood, but the rest of the material is unaffected.

CHAPTER XX

ABEL ON THE STORAGE OF GUNCOTTON (1867)¹

THE conclusions drawn from the experiments were as follows:

(1) Guncotton closely packed in metal-lined cases, of considerable size, in two of which some imperfectly prepared guncotton was purposely included, sustained uniformly a daily exposure for twelve hours during three months to a heated atmosphere, the temperature of which generally ranged from 49° to 51° C. for a period of seven hours, without furnishing any indication of the development of heat within the mass of the guncotton consequent upon chemical change.

(2) The further exposure of these packages for another period of three months to a heated atmosphere, the temperature of which generally ranged during seven hours daily between 54° C. and 55° C., resulted only in *one* instance in the development of heat in the guncotton; and the particular box which, at the expiration of six months' treatment, furnished this indication that its contents were undergoing decomposition, was filled with guncotton in the condition which all previous experiments had indicated as least capable of resisting the effects of prolonged exposure to heat; being, namely, almost free from substances (carbonates) which would exert a neutralizing action upon any acid generated by decomposition of the comparatively unstable impurities existing in the guncotton.

(3) The box which next furnished very slight indications of the development of heat, after exposure for six and a half months, contained guncotton through which a small proportion of earthy carbonates had been distributed by its submission to the so-called "silicating process," but in the centre of which a specimen of imperfectly purified guncotton had been packed. There is no question that this box would have furnished much earlier indications of the occurrence of chemical change in its contents, if the guncotton principally composing the latter had not been protected for a considerable period, by the presence of

¹ *Trans. Roy. Soc.* (1867), 181-253.

onates, from the destructive effects of acid liberated from imperfectly purified guncotton which was packed in the crevice of the box.

4) A box of "silicated" guncotton containing a small quantity of soluble guncotton not silicated, was the next to exhibit symptoms of decomposition after having been exposed at for seven months. Numerous experiments have shown the soluble guncotton is not more prone to decomposition than the most perfectly converted material; but the sample placed in the centre of this box was not protected by carbonates, therefore doubtless sustained change considerably sooner than the chief portion of the contents of this box, promoting deterioration in the latter, after the lapse of some time, when the protective effect of the carbonate had become neutralized.

5) The box which was entirely filled with guncotton, prepared strictly according to von Lenk's system, including its admission to the "silicating" process, only exhibited a slight indication of internal development of heat after having been sealed for eight months to a heated atmosphere. The protective effect exerted by the small proportion of earthy carbonate situated in the guncotton as a result of the "silicating" treatment was, in this instance, not diminished by the presence of any guncotton not thus treated, and consequently the contents of this box resisted change for a longer period than the "silicated" guncotton in the two other boxes (2 and 3). Moreover, this guncotton, though exposed to heat for two months longer than the unsilicated guncotton (in No. 1 box), was found on examination to have evolved considerably less acid.

6) The guncotton which had been uniformly impregnated with only 0.3 per cent. of sodium carbonate furnished no signs of development of heat up to the period when the experiment was interrupted, having been, at that time, exposed for seven months to a heated atmosphere, the temperature of which ranged, for seven hours daily, for seven months, between 25° and 55° C. It is much to be regretted that a careful examination of the contents of this box after so prolonged and complete an exposure to heat was prevented by an accident.

7) The condition of the guncotton after exposure to heat in the three boxes first removed was very similar. Although the material was found to be highly impregnated with nitric and nitrous acid (the development of which there is every

reason to believe had been very considerably promoted by the large metal surfaces of the boxes which were in close contact with the guncotton), the decomposition had not proceeded in any one of the boxes to such an extent as to produce an alteration in the explosive and other properties of the guncotton. When the latter had been purified from the free acid developed in it, no difference could be discovered between it and the original material, except that it had become slightly bleached. The guncotton from boxes 1 and 4, after being purified by digestion in alkaline water and subsequent repeated washing in distilled water, was dried, repacked and returned to the hot-air chamber. It now contained no carbonates whatever by which the destructive effect of acid, if developed, could be retarded or prevented; but the boxes, each containing eleven pounds of this guncotton, were exposed to heat for three months, the temperature of the air ranging from 54° to 55.5° C. for seven hours daily, and no indication whatever of development of heat was obtained in either instance. (The purified guncotton from boxes 3 and 4 was also repacked and returned to the chamber at later periods.) After the heat experiments described above had been continued between eight and nine months, two barrels, fitted with tubes for thermometers, each containing about twenty-three pounds of guncotton which was neither "silicated" nor impregnated with sodium carbonate, were placed in the chamber, the object being to obtain direct proof of the extent of the influence exerted by the metal surfaces in the cases employed in the other experiments, upon the behaviour of the guncotton itself. Two other much smaller metal lined cases, each containing about five pounds of guncotton, were also placed in the chamber at this time; one of them was filled with a sample which had already been subjected to severe exposure to heat and had subsequently been purified from acid, and the other was filled with discs prepared by compressing guncotton which had been reduced to pulp. Lastly, an ammunition case containing twenty-three pounds of guncotton, which was impregnated with a more considerable quantity of sodium carbonate than was employed in the first experiment, was added to the contents of the chamber. The heating of the latter to 54° - 55° C. was continued for about six weeks when an explosion occurred, which destroyed the chamber and the whole of the samples, excepting some of the compressed guncotton.

As is generally the case in accidents of this kind, the immediate cause of the explosion could not be traced with certainty. The usual periodical readings of the thermometers enclosed in the packages had been taken shortly before the explosion occurred, and all the temperatures last recorded were below that of the air in the chamber, which had been at 55.5°C . from two till six o'clock; not one of the packages had furnished any indication that heat was developed, but the temperature in the two small boxes was considerably higher than in the large packages; the comparatively small volume of guncotton became much more rapidly heated throughout, so that the temperature recorded in these instances at the close of the day's heating was generally within 2°C . of the maximum external temperature. It appears most probable, therefore, that the small parcel of guncotton which had already suffered some change by exposure to heat, and which had since been exposed for six weeks to a heated atmosphere ranging between 52°C . and 55.5°C . for seven hours daily, eventually sustained further alteration, which, though very gradual for a time, at length increased to such an extent that heat was very rapidly developed, raising the guncotton to the temperature required for its explosion within a comparatively brief period. The experiments made at 100°C . with small quantities of guncotton which have been described in an early part of this paper, demonstrated that, when once a considerable decomposition of the substance had set in, the development of heat was very rapid indeed. It was believed, however, that the *first* establishment of decomposition would in all instances be indicated by so gradual a rise of temperature that frequent periodical observations of a thermometer placed in the centre of packages of heated guncotton would always afford the means of carrying on experiments of this class with security, a belief which was strongly supported by the results of the experiments carried on for periods of five, six, and ten months with five large packages of guncotton. The power to resist serious decomposition upon continued exposure to a highly heated atmosphere had proved so unexpectedly great in the case of every one of those experiments, that it was considered important to ascertain, if possible, the full extent of those powers. Hence, with what proved to be undue reliance upon the infallibility of the measures adopted to guard against accidents, the experiments were protracted

and the variety of tests increased, far beyond the extreme limits necessary for the attainment of their original object, which was to ascertain how far guncotton either of ordinary manufacture, or accidentally defective or protected by special preparation, would resist change under conditions representing the extremes, both in extent and duration, of heat to which it might be exposed if stored or used in active military service in tropical climates.

The Committee on Guncotton has endeavoured to collect reliable data with reference to the average and extreme temperatures to which guncotton might be exposed in ships' magazines during the passage of vessels through tropical regions, or to which it might be subject in India if directly exposed to the sun in ammunition boxes; these being the most severe natural conditions of exposure to heat which would ever be likely to occur. A statement was furnished to General Sabine, by the late Admiral Fitzroy, of the maximum and minimum temperatures recorded monthly in the chronometer room of Her Majesty's Ship *Odin*, between September 1861 and September 1863, this vessel having been during that period at Japan, in the China Sea, Malacca Strait, Indian Ocean, Bengal Bay, North and South Atlantic, etc. The highest temperatures recorded were in May 1862 and April 1863 (in the Indian Ocean), being 31° C. on both occasions; the minimum temperatures in those months were 29° C. and 26.8° C. Between February 1862 and August 1863 the registered maximum temperatures ranged between 25.3° C. and 31° C., and the minimum temperatures between 14.7° C. and 29° C. Admiral Fitzroy considered that, except at times when the men were continuously at work in a ship's magazine, the temperature within the latter would be regulated by that of the surrounding water, which, at a few feet below the surface, is never warmer than from 26° to 30° C. If this is the case, the temperature records obtained from the *Odin* afford a fair representation of the maximum and minimum temperatures of the atmosphere in magazines where guncotton might be stored on board ship. Steps have, however, been taken to obtain records of the maximum and minimum temperatures actually experienced in ships' magazines.

At the request of General Sabine, Mr. Pogson, the Astronomer at Madras, took daily readings, from 1st May to 30th June 1866, of thermometers placed in boxes, the one painted black and the other white, and both exposed to the sun. The

complete account of the observations made by that gentleman has not yet been received, but in a letter to General Sabine, he states that during the above-named period, which occurred in the hottest and driest season ever experienced in Madras, the highest temperature registered inside the black box was $51.2^{\circ}\text{C}.$, that in the white box being $44^{\circ}\text{C}.$, whilst the lowest minimum readings recorded were $26.8^{\circ}\text{C}.$ in the black box and $26.1^{\circ}\text{C}.$ in the white box. The maximum temperature recorded in the empty black box, exposed to the sun at Madras, was therefore about $5^{\circ}\text{C}.$ below the average temperature to which closely-packed guncotton, in a condition most favourable to change, was exposed for about seven hours daily, during three months (having previously been similarly exposed to an atmosphere at $50^{\circ}\text{C}.$ for an equal period), before there was any indication of development of heat, while guncotton prepared according to von Lenk's directions resisted a similar exposure for five months, and ordinary guncotton, containing a small proportion of sodium carbonate, furnished no indication of change when it had been stored under the same circumstances for seven months.

General Morin, in some observations upon the recent report of Pelouze and Maury on guncotton, referred to the existence of instances in which the atmosphere in the interior of buildings had been raised to a temperature of $38^{\circ}\text{C}.$, $40^{\circ}\text{C}.$ or $42^{\circ}\text{C}.$ (the external atmosphere being only $21^{\circ}\text{C}.$) by the passage of solar heat through glass windows or roofs, and also stated that it was not uncommon to find the interior of powder-wagons, covered with metal, at a temperature of 50° - $60^{\circ}\text{C}.$, while the external temperature was only $24^{\circ}\text{C}.$ It is evident from the nature of this statement that the elevation of temperature to this extent in the localities described was only transient; but even if the atmosphere in magazines or ammunition-wagons were occasionally at such temperatures for several consecutive hours during a considerable period, it may be confidently maintained that guncotton, properly purified and impregnated with a small proportion of sodium carbonate, as has been described, may be preserved in such localities with perfect safety, even in a closely-packed condition. It has been shown that guncotton, even without the aid of the very decided though variable protection afforded to it by the "silicating" process, sustained no change whatever by continuous exposure to the sun's rays in a black box between April and September, the temperature of

the external surface of the box having frequently exceeded 40° C., and that the same kind of guncotton sustained, without any change, three months' exposure for several hours daily to an atmosphere of 50° C., and did not exhibit any indication of change until after further exposure for nearly three months to an atmosphere maintained for several hours daily at 54.5° - 55.5° C. In both these instances the guncotton was as closely packed as possible in one mass (and in the latter it was contained in a case lined with tinned copper which seriously influenced the effect of heat upon the guncotton). It is therefore considered that the extent and circumstances of exposure to heat which even this perfectly unprotected guncotton resisted, may be regarded as exceeding in severity such as it would have to encounter in the actual employment of the material in naval and military service.

CHAPTER XXI

ABEL'S PRINCIPAL CONCLUSIONS ON GUNCOTTON (1867)¹

(1) GUNCOTTON produced from properly purified cotton, according to the directions given by von Lenk, may be exposed to diffused daylight, either in the open air or in closed vessels, for very long periods without undergoing any change. The preservation of the material for $3\frac{1}{2}$ years under those conditions has been perfect.

(2) Long-continued exposure of the substance, in a condition of ordinary dryness, to strong daylight and sunlight produces a very gradual change in guncotton of the description defined above; and the statements which have been published regarding the very rapid decomposition of guncotton when exposed to sunlight do not therefore apply to the nearly pure trinitrocellulose obtained by strictly following the system of manufacture now adopted.

(3) If guncotton in closed vessels is left for protracted periods exposed to strong daylight in a moist or damp condition, it is affected to a somewhat greater extent; but even under these circumstances the change produced in the guncotton by several months' exposure is of a very trifling nature.

(4) Guncotton which is exposed to sunlight until a faint acid reaction has become developed, and is then immediately afterwards packed into boxes which are tightly closed, does not undergo any change during subsequent preservation in ordinary storehouses (as far as the experience of $3\frac{1}{2}$ years has shown).

(5) Guncotton prepared and purified according to the prescribed system, and stored in the ordinarily dry condition, does not furnish any indication of alteration, beyond the development, shortly after it is first packed, of a slight peculiar odour, and the power of gradually imparting to litmus, when packed with it, a pink tinge.

(6) The influence exercised upon the stability of guncotton of average quality, as obtained by strict adherence to von Lenk's

¹ *Trans. Roy. Soc.* (1867), 181-253.

system of manufacture, by prolonged exposure to temperatures considerably exceeding those which are experienced in tropical climates, is very trifling in comparison with the results recently published by continental experimenters relating to the effects of heat upon guncotton; and it may be so perfectly counteracted by very simple means, which in no way interfere with the essential qualities of the material, that the storage and transport of guncotton presents no greater danger, and is, under some circumstances, attended with much less risk of accident than is the case with gunpowder.

(7) Perfectly pure guncotton, or trinitrocellulose, resists to a remarkable extent the destructive effects of temperatures even approaching 100° C., and the lower nitro-products of cellulose (soluble guncotton) are, at any rate, not more prone to alteration, when pure. The incomplete conversion of cotton into the most explosive product does not, therefore, of necessity result in the production of a less perfectly permanent compound than that obtained by the most perfect action of the acid mixture.

(8) But all ordinary products of manufacture contain small proportions of nitrogenized organic impurities, of comparatively unstable properties, which have been formed by the action of nitric acid upon foreign matter retained by the cotton fibre, and which are not completely separated by the ordinary or even by a more searching process of purification. It is the presence of this class of impurity in guncotton which first gives rise to the development of free acid, when the substance is exposed to the action of heat; and it is the acid thus generated which eventually exerts a destructive action upon the cellulose products, and thus establishes decomposition, which heat materially accelerates. If the small quantity of acid developed from the impurity in question be neutralized as it becomes nascent, no injurious action upon the guncotton results, and the great promoting cause of the decomposition of guncotton by heat is removed. This result is readily attained by uniformly distributing through guncotton a small proportion of a carbonate, sodium carbonate applied in the form of solution being best adapted to this purpose.

(9) The introduction into the finished guncotton of 1 per cent. of sodium carbonate affords to the material the power of resisting any serious change, even when exposed to such elevated

temperatures as would induce some decomposition in the perfectly pure cellulose products. That proportion affords, therefore, security to guncotton against any destructive effects of the highest temperatures to which it is likely to be exposed, even under very exceptional climatic conditions. The only influences which the addition of that amount of carbonate to guncotton might exert upon its properties as an explosive, would consist in a trifling addition to the small amount of smoke attending its combustion, and in a slight retardation of its explosion, neither of which could be regarded as results detrimental to the probable value of the material.

(10) Water acts as a most perfect protective to guncotton (except when it is exposed to sunlight), even under extremely severe conditions of exposure to heat. An atmosphere saturated with aqueous vapours suffices to protect it from change at elevated temperatures, and wet or damp guncotton may be exposed for long periods in confined spaces to 100° C. without sustaining any change.

Actual immersion in water is not necessary for the most perfect preservation of guncotton; the material, if only damp to the touch, sustains not the slightest change, even if closely packed in large quantities. The organic impurities which doubtless give rise to the very slight development of acid observed when guncotton is closely packed in the dry condition, appear equally protected by the water; for damp and wet guncotton which has been preserved for three years has not exhibited the faintest acidity. If as much water as possible be expelled from wet guncotton by the centrifugal extractor, it is obtained in a condition in which, though only damp to the touch, it is perfectly non-explosive; the water thus left in the material is sufficient not only to act as a perfect protective, but also to guard against all risk of accident.

CHAPTER XXII

SOBRERO'S DISCOVERY OF NITROGLYCERIN (1847)

ASCANIO SOBRERO, Professor of Chemistry in Turin, was born October 12, 1812, at Casale, and died in Turin, May 26, 1888. His discovery of nitroglycerin was communicated to the Academy of Science in Turin in a paper dated February 21, 1847, and entitled *Some new fulminating products obtained by the action of nitric acid on some vegetable organic substances*.¹ Sobrero had already shown that the action of nitric acid upon sugar, dextrine, lactine and mannite produced bodies of an explosive character, but he was surprised to find that glycerin, when nitrated, produced a violently explosive body.

"Glycerin, under certain circumstances, is very readily oxidized. Nitric acid reacts on it very energetically, producing oxalic acid, and, in all probability, intermediate compounds of a more complicated nature are formed. If concentrated nitric acid or a mixture of two volumes of sulphuric acid of 1.84 sp. gr. and one volume of nitric acid of 1.5 sp. gr. is added to glycerin, concentrated to a syrupy condition, a very violent reaction is set up, with the evolution of very considerable quantities of oxides of nitrogen. If, however, we reverse the process and pour the glycerin into a mixture of the acids kept at a temperature of several degrees below zero, the reaction is quite different. The glycerin goes into solution in the mixed acids, and with greater readiness by constant stirring. When the glycerin has been completely dissolved, the contents of the vessel are poured into distilled water at the ordinary temperature. Drops of an oily liquid immediately collect at the bottom of the vessel containing the water, and finally join together to form a distinct layer. This oily liquid is a new compound which I propose to call *Piroglycerina*. (Hereafter nitroglycerin will be used instead of Sobrero's original name.) Nitroglycerin can be readily freed from adherent acid by washing with water, in which it is insoluble, and, on placing

¹ *Torino. Mem. Acad.* (1847), 195-203.

it in a vacuum over sulphuric acid, the traces of adherent water are absorbed and a transparent liquid obtained. It is of a light yellow colour, highly refractive, and remains liquid down to a temperature of -20° C. It is soluble in alcohol and in ether and may be obtained in a high state of purity by dissolving it in alcohol and reprecipitating with water, or by allowing its ethereal solution to evaporate spontaneously. The properties of nitroglycerin are very remarkable. It has a specific gravity of 1.6 at 10° C. When traces of water are present it loses its transparency. Bodies which are easily oxidized rapidly decompose nitroglycerin. It detonates when brought into contact with metallic potassium, and evolves oxides of nitrogen in contact with phosphorus at 20° to 30° C., but at higher temperatures it ignites with an explosion. Copper is oxidized by it with the production of oxides of nitrogen. It is not attacked by concentrated sulphuric acid or nitric acid to any marked extent, and aqua regia only acts on it when heated. It decomposes hydrochloric acid with the production of chlorine, and becomes of a yellow colour on the addition of strong bases. Caustic potash decomposes it, when heated, producing ammonia. When heated, nitroglycerin decomposes. A drop heated on platinum foil ignites and burns very fiercely. It has, however, the property of detonating, under certain circumstances, with great violence. On one occasion a small quantity of an ethereal solution of nitroglycerin was allowed to evaporate in a glass dish. The residue of nitroglycerin was certainly not more than 2 or 3 centigrams. On heating the dish over a spirit lamp a most violent explosion resulted, and the dish was broken to atoms. On another occasion a drop contained in a test tube was being heated when it detonated with great violence, and pieces of glass cut my face and hands severely and also injured others standing some distance away in the room. The safest plan for demonstrating the explosive power of nitroglycerin is to place a drop upon a watch glass and detonate it by touching it with a piece of platinum wire heated to low redness. Nitroglycerin has a sharp, sweet, aromatic taste. It is advisable to take great care in testing this property. A trace of nitroglycerin placed upon the tongue, but not swallowed, gives rise to a most violent, pulsating headache, accompanied by great weakness of the limbs. A dog was given a few centigrams of nitroglycerin. It soon after began to foam at the mouth and

then vomited. Despite the fact that the greater part of the nitroglycerin had thus been eliminated from the system, within seven or eight minutes the animal had fallen down and almost ceased breathing. A dose of olive oil and ammonia was then administered. The animal revived somewhat, and remained for some two hours, whining, trembling violently, and beating its head on the wall. A *post-mortem* examination showed that the vessels of the brain and heart were suffused with blood and much distended. Similar results were obtained with rats and guinea-pigs. The violence of the decomposition of nitroglycerin has prevented me, up to the present, making an analysis of this body. One experiment in this direction resulted in the violent ejection of the copper oxide from the combustion tube. On theoretical grounds, seeing that it is made in a similar manner to other explosive bodies, such as nitromannite, etc., I am inclined to think that it is produced by the replacing of two equivalents of water by two equivalents of the anhydride of nitric acid. As no residue remains after detonation, it follows that nitroglycerin is converted, on decomposition, entirely into gases. If this body be considered as a nitrate of glycerin, it might perhaps be possible to produce, by double decomposition, a new series of compounds of the fatty acids with glycerin. I have made some experiments in this direction by heating nitroglycerin with a soap solution, but have not been able in this way to produce an oleate. It is perhaps possible that an intermediate compound is produced by the elimination of one of the nitric acid groups. The explosive compounds obtained from lactine and mannite are very similar to nitrosugar which I have previously prepared. They are both soluble in alcohol and ether and insoluble in water. Nitromannite crystallizes in small needles, whilst the other compound is amorphous. Like nitrosugar they liquefy when heated gently and decompose without explosion. They, however, explode when rapidly heated to a high temperature."

Sobrero adds a further note some five months later:—

"The greater number of these explosive bodies have shown themselves to be unstable. It is only a question of a longer or shorter time before they begin to decompose with production of nitrogen dioxide. The nitro-compounds of sugar, lactine and dextrine all behave in this manner. Nitromannite, alone, during the course of four months appears to show a perfect

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stability. Nitroglycerin kept below water is covered, after some months, with little bubbles of gas which I believe to be nitrogen dioxide. It is perhaps hardly necessary to add that heat favours this decomposition. The nitro-compounds of sugar and lactine which appeared to be stable during the winter months began to show signs of decomposition during the greater heat of summer. It remains to be added that water, standing for a month in contact with nitroglycerin, besides being acidic, showed very distinct traces of the presence of cyanogen."

CHAPTER XXIII

NITROGLYCERIN IN HOLLAND AND ENGLAND (1855)

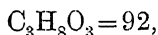
AN examination of Sobrero's published researches, after his discovery of nitroglycerin, shows no record of his having again worked on the subject. He lived, however, to see nitroglycerin raised, by the genius and perseverance of Nobel, to the position of first importance as a constituent of modern explosives. The next work on the subject was by J. E. de Vrij, Professor of Chemistry at the School of Medicine in Rotterdam. The physiological effects of nitroglycerin led him to prepare this body and to repeat some of Sobrero's experiments. In 1851 he communicated some of his results to the British Association for the Advancement of Science, and the Proceedings of that year contain the following note: "This yellow liquid, nitroglycerin, seems not to be poisonous, but it explodes at a moderate heat, detonating when the drops of nitroglycerin on paper were struck a smart blow with a hammer." De Vrij published a full account of his work in the Dutch Journal of Pharmacy in 1855 in a paper entitled *Nitroglycerin or Glonoïne*.

"In 1847, when guncotton occupied the attention of all chemists, Sobrero discovered that glycerin, treated by a mixture of sulphuric and nitric acids, gave an analogous compound. He thus obtained an oleaginous substance, heavier than water, almost insoluble in that liquid, but soluble in ether and in alcohol. According to the author, the smallest quantity of this liquid occasioned violent headache, whence he concluded that it was a very violent poison. These properties attracted my attention and I endeavoured in 1851 to make this substance. My experiments on a small scale were perfectly satisfactory, and enabled me partly to confirm Sobrero's observations, especially the property possessed by nitroglycerin of producing headache; but, at the same time, I found it could not be a violent poison, since ten drops of this substance administered to a rabbit did not produce any very evident symptoms of poisoning.

¹ *Tijdschrift voor wetensch pharm.* (1855).

The desire to know the composition of nitroglycerin determined me to prepare a large quantity of it. These fresh experiments had the unfortunate result of depriving me of sight for a long time in consequence of an explosion of the mixture. After my recovery, I resumed my investigations and prepared a considerable quantity of nitroglycerin, and ascertained several of its properties which I communicated in the summer of 1851 to the British Association. I then left the subject, until my attention was again called to this product by some articles in the foreign journals, from which I learned that nitroglycerin is now used as a medicine in America under the name of 'Glonoine.' Besides the interest attached to this product from a chemical point of view, it has, therefore, acquired a pharmaceutical value. This determined me to make known the mode of its preparation and its principal properties. After various trials I prefer the following mode of preparation: 100 grms. of glycerin, as far as possible deprived of water at 150°C ., and having a sp. gr. of 1.262, were added by degrees to 200 cc. of strong nitric acid, placed in a refrigerating mixture. At each addition of glycerin the temperature rose and I waited till it descended to 0°C . It is necessary to take care during the solution of glycerin in nitric acid that the temperature should be always below 0°C . The mixture was stirred with a glass rod, and, when the glycerin and acid had formed a homogeneous liquid, 200 cc. of concentrated sulphuric acid were added in small portions at a time. This part of the operation presents the most danger if continued attention is not paid to the temperature. Experience has taught me that there is no danger if the temperature does not exceed 0°C . I once saw the temperature rise as high as 10°C ., but between that and 20°C . there was a sudden and violent reaction between the glycerin and the nitric acid, in consequence of which the liquid was violently projected out of the vessel. This inconvenience is completely avoided by keeping the temperature below 0°C . With this precaution the nitroglycerin, after the addition of sulphuric acid, separated in the form of an oil floating on the surface of the acid and was removed by means of a funnel with a tap. The quantity of this impure product, containing a little acid, amounted to 200 grms. I produced about 20 grms. more by mixing with water the acid which had separated from it. These 220 grms. were then dissolved in as small a quantity of ether as possible, and the solution

was agitated several times with cold water, until it no longer reddened litmus. It was then evaporated on a sand-bath and heated until the nitroglycerin no longer lost weight. The quantity of pure product thus obtained amounted to 184 grms. The composition of glycerin is



so that the yield of 184 grms. from 100 grms. of glycerin leads us to presume that the composition of nitroglycerin would be represented by



I am now engaged in trying to ascertain whether this composition is correct.

The properties of nitroglycerin are as follows. It is a pale yellow oleaginous liquid with a density of 1.595-1.600 at the ordinary temperature. Heated to 160° C. it decomposes, disengaging red vapours. At a higher temperature it explodes, breaking the vessel in which it is contained, or else it inflames without detonating. I do not know the precise temperature at which this detonation takes place. It will be best observed by heating a porcelain plate, removing it from the fire, and dropping a little nitroglycerin on it occasionally. As long as the temperature continues too high it burns with an intense flame; but as the temperature falls, the nitroglycerin, as it strikes the plate, disengages thick vapours and detonates with great violence, breaking the plate. Detonation is always produced when nitroglycerin is struck with a hammer on an anvil. When properly prepared, and free from acid, it forms a very constant compound. I have now some nitroglycerin which has been prepared for more than two years, and still remains quite unaltered. Sulphuretted hydrogen decomposes the ethereal solution and separates from it a large quantity of sulphur. The products of this reaction, which I am now studying, will perhaps throw some light on the composition of nitroglycerin."

De Vrij's method of preparation would naturally tend to give him low yields, and this fact misled him as to the composition of nitroglycerin. He must have been using an impure sample of nitroglycerin when he states that, in ethereal solution, it reduces sulphuretted hydrogen to sulphur.

The first analysis of nitroglycerin was made by Robert Railton, who in 1855 communicated a paper to the Chemical

Society, London, entitled *On nitroglycerin and the products of its decomposition by potash*.¹

"Sobrero discovered nitroglycerin but did not determine its composition. The compound from which the following results were obtained was thus prepared. Equal volumes of concentrated nitric and sulphuric acids were mixed and cooled in ice-cold water. Syrupy glycerin was introduced, a few drops at a time, shaken, and cooled each time. After some time the product floated on top, as an oily liquid. It was then poured into cold distilled water and repeatedly washed in this menstruum by decantation. It was afterwards freed as much as possible from water by means of blotting-paper, and an attempt was made to dry it more completely under the bell-jar of an air-pump, but without success, as it was rapidly decomposed on exhausting the jar. From this circumstance the hydrogen could not be estimated, but the relative amounts of carbon and nitrogen were satisfactorily determined by Liebig's process. About 1 gr. of nitroglycerin was mixed with as much copper oxide as half filled a combustion tube, about 36 inches long. About 8 inches of the remainder of the tube were filled with copper oxide and the remainder of the tube was then wholly filled with reduced copper. The tube was then enveloped in copper foil and the combustion proceeded with, and the mixed gases collected in a graduated tube over mercury. The first portion of the gas was allowed to escape. Four tubes were filled, and the following are the results in the order in which they were collected:—

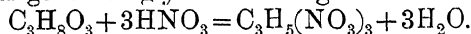
	I.	II.	III.	IV.
Volume of Mixed Gases	101	91.5	99	97
Volume absorbed by Caustic Potash	69	61.0	65	64
Volume remaining unabsorbed	32	30.5	34	33

There being slight discrepancies in these results, I obtained tubes more finely divided, when a second experiment gave:—

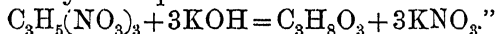
	I.	II.	III.	IV.	V.
Volume of Mixed Gases	179	194	192	173	194
Volume absorbed by Caustic Potash	117	128	127	115	129
Volume remaining unabsorbed	62	66	65	58	65

¹ *Qr. J.C.S.* (1855), 222.

Now, as the composition of glycerin is well known, and as the volume of nitrogen is proved to be half that of the carbon dioxide absorbed by potash, we may safely assume the following to be the change which glycerin undergoes:—



Nitroglycerin, when boiled for some time with an aqueous solution of potash, is decomposed. Potassium nitrate and glycerin are formed. A solution of caustic potash in water was made of nearly the same sp. gr. as nitroglycerin. The mixture was boiled for several hours. At the end, the liquid became completely homogeneous when it was carefully neutralized with pure sulphuric acid. The potassium sulphate was crystallized out and on further evaporation potassium nitrate was deposited. This salt was purified by repeated crystallization and afterwards analyzed as sulphate. For the purpose of obtaining the glycerin, the solution from which the potassium nitrate had been crystallized out was evaporated to a syrupy condition and treated with absolute alcohol. The solution of glycerin in alcohol thus obtained was evaporated in a water-bath, and the residue treated with ether, in which nitroglycerin, had there been any undecomposed, would have been dissolved. The ether was removed, without having dissolved anything, and a portion of the residue was heated with acid potassium sulphate, when the pungent odour of acrolein was evolved. The decomposition of nitroglycerin by means of caustic potash may thus be represented by the equation—



It is rather a remarkable fact that 32 years elapsed, from the date of the publication of Railton's paper, before the composition of nitroglycerin was satisfactorily established. Several workers had determined the percentage of nitrogen in nitroglycerin, with very varying results. Railton's explanation of the mode of decomposition of nitroglycerin by potash was also accepted, in the main, as correct. It was not until 1887 that Hay and Orme Masson published in the *Transactions of the Royal Society of Edinburgh*, a very complete investigation of the composition of nitroglycerin, and showed that Railton's formula for the decomposition of nitroglycerin by potash was not correct.

CHAPTER XXIV

NOBEL'S PATENTS FOR THE MANUFACTURE AND DETONATION OF NITROGLYCERIN (1864), DYNAMITE (1867), STRAIGHT DYNAMITE (1869), BLASTING GELATINE AND GELIGNITE (1875), AND BALLISTITE (1888)

ALFRED NOBEL was born at Stockholm on 21st October 1833, and died on 10th December 1896. Although Sobrero's discovery of nitroglycerin dated back to 1847, this explosive was manufactured on a commercial scale for the first time in 1862 by Nobel, at a factory which he erected at Heleneborg, near Stockholm. These works were entirely wrecked by an explosion in 1864. In 1865 he erected works, which are still in existence, at Winterviken, near Stockholm. In 1864 Nobel introduced modifications in the manufacture of nitroglycerin which were the subject of a patent,¹ and, at the same time, claimed a process for the detonation of nitroglycerin. Nobel states that, up to that time, the method used for the manufacture of nitroglycerin consisted in pouring glycerin, drop by drop, into a mixture of sulphuric acid and nitric acid contained in a refrigerating mixture. In order that the nitroglycerin should not be decomposed the temperature was not allowed to rise above 0° C. Nobel proposed the following modification, by which the yield was increased. After mixing the glycerin and sulphuric acid together, nitric acid was added gradually, so that the temperature after each addition never rose above 4.5° C. He found that if, after separation of the nitroglycerin, the nitrating acids were cooled to 5-10° C., a further quantity of nitroglycerin was crystallized out, and that then the nitric acid and sulphuric acid could be recovered by denitration and concentration. As a rapid method for the preparation of nitroglycerin he suggested using a mixture of 2 parts of sulphuric acid and 1 part of nitric acid, adding the whole of the glycerin immediately, stirring rapidly, and pouring instantly into cold water. Despite the high temperature developed, very little of the nitroglycerin

¹ British Patent (1864), 1813.

was decomposed. Instead of sulphuric acid the use of the monohydrate of phosphoric acid was suggested.

No liquid explosive body had been used for industrial purposes, and Nobel claimed that he was the first to effect a practical solution of the problem. He showed that it was sufficient to produce an initiative explosion which then spread through the mass. The following methods of bringing about this initial impulse were suggested. The nitroglycerin might be contained in an open vessel in which was suspended a small glass vessel containing gunpowder or other explosive. As a means of producing sufficient heat to ignite the gunpowder he suggested separate vessels containing, on the one hand, either sulphuric acid or quicklime, and, on the other hand, water. Another method suggested was an electric spark or a wire heated by an electric current, provided that they were applied in the interior of the nitroglycerin; and, finally, there was the proposal of a percussion cap. We thus have, in these claims, the fundamental idea of the detonation of explosives, which developed later into the use of the detonator and the electric detonator, and immediately placed the use of nitroglycerin as a blasting agent, in the form of dynamite, upon a practical basis.

Nobel's real troubles were now, however, only beginning. The explosion at the Heleneborg works, in which his youngest brother perished, the alarming explosions with nitroglycerin in its liquid state, the absolute prohibition by some countries, and the restrictions imposed by others as to its manufacture and transport, were obstacles sufficient to have daunted the stoutest heart. Still Nobel persevered, and recognising that nitroglycerin in its liquid state was impracticable, his investigations to overcome this defect led him to the discovery of *Dynamite*.¹ The nitroglycerin was absorbed in porous non-explosive substances, such as charcoal, silica, paper, etc., and was thus converted into a powder which was called Dynamite, or Nobel's Safety Powder. Nitroglycerin thus acquired the property of being in a high degree non-sensitive to shock. He eventually utilized kieselguhr, which was then employed in his Krummel factory for packing the tins of nitroglycerin in wooden boxes.² Dynamite, according to Nobel, could be exploded when under very close confinement by means of a spark, or any mode of ignition

¹ British Patent (1867), 1345.

² H. de Mosenthal, J.S.C.I. (1899), 444.

used for firing gunpowder. Under any conditions it could be exploded by means of a special cap containing a strong charge of fulminate adapted to the end of the fuse and strongly squeezed upon it for the purpose of more effectively confining the charge and heightening the effect of detonation. He states that the fulminate cap could be greatly varied in form, but that the principle of its action lay in the sudden development of a very intense pressure or shock. The porous substance, before it was saturated with nitroglycerin, could be rendered alkaline with sodium carbonate in order to ensure the more perfect stability of the explosive.

The next important step in Nobel's investigations was reached in 1869 with the discovery of *Dynamite with an active base*,¹ in which the absorbent consisted of wood-meal, and potassium, sodium or ammonium nitrates, and he proposed to overcome the defect of the hygroscopic nature of these two last salts by adding paraffin or ozokerite. Explosives of this nature are manufactured very largely in the United States, Canada and Mexico, under the name of "Straight Dynamites," but have never been used in Great Britain, as they do not satisfy the requirements of the Home Office tests for nitroglycerin explosives.

Dissatisfaction with dynamite on account of its 25 per cent. of inert material, and with dynamite with an active base on account of the insufficient retention of nitroglycerin, led Nobel to further work, resulting in the discovery of *Blasting Gelatine* and *Gelignite*.² He found that nitroglycerin could be gelatinized by dissolving in it nitrated cellulose, known as collodion guncotton. The explosive compound became more and more gelatinous in proportion to the quantity of nitrated cellulose dissolved in the nitroglycerin, and when from 7 to 8 per cent. was present a solid jelly was formed which was found to be highly suitable as a powerful explosive. The incorporation was facilitated by means of special treatment which consisted in adding small quantities of substances which promoted the gelatinization, such as acetone, ether and alcohol, nitrobenzene, methyl and ethyl nitrates, etc., but Nobel stated that by gently heating nitroglycerin on the water-bath it acquired the property of dissolving nitrated collodion cellulose without the addition

¹ British Patent (1869), 442.

² British Patent (1875), 4179.

of any promoting solvent. He pointed out the care that should be exercised in the selection of a suitable collodion cotton and that the process of incorporation was facilitated by mechanical stirring or kneading.

To prepare a cheaper explosive of lesser power he suggested adding to his gelatinized nitroglycerin such substances as gunpowder and various mixtures of nitrates and chlorates, with coal dust, sulphur, sugar, starch, sawdust, resin and fatty matters. With the proposed addition of a nitrate and sawdust to gelatinized nitroglycerin we thus arrive at Nobel's discovery of *Gelignite*.

Nobel's next astonishing achievement was the invention of *Ballistite*.¹ It is evident from his specification that the study of celluloid led him to the remarkable invention of the production of a propellant from the two most powerful explosives known. He found that by replacing almost the whole of the camphor in celluloid by nitroglycerin, a material could be obtained which was suitable as a propellant. The composition and method of manufacture of the explosive are given as follows. Camphor (10 parts) is dissolved in nitroglycerin (100 parts). Benzene (200 parts) is added, and then 50 per cent. of dry pulped soluble cellulose nitrate. After incorporation the benzene was allowed to evaporate and the mass was kneaded between hot rollers, so as to form a sheet. Nobel discovered very shortly afterwards that, when using soluble collodion cotton, he could dispense entirely with both camphor and solvents, and that ballistite could be manufactured from its two ingredients by means of heat and malaxation alone.

The discovery of the detonation of nitroglycerin by fulminate, the invention of Dynamite, Straight Dynamite, Blasting Gelatine, Gelignite and Ballistite are, in themselves, a remarkable achievement; but when we know that Nobel made, in all, 122 applications for British patents, many of them wholly unconnected with explosives, the fertility of his inventive genius is a subject for admiration and astonishment. Nobel's dauntless courage, born of genius and the clear flame of science, combined with a perfect grasp of technology, places him in a position of undoubted supremacy amidst the great master minds in the industry of modern explosives.

¹ British Patent (1888), 1471.

SOME OF NOBEL'S PATENTS

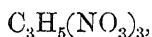
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[A very complete account of the lifework of Nobel is given by Mr. H. de Mosenthal in the *Journal of the Society of Chemical Industry* (1899), 443-451, and the present writer expresses his indebtedness to the author for much of the data appearing in the foregoing paper.]

CHAPTER XXV

THE ANALYSIS AND COMPOSITION OF NITROGLYCERIN

IN a previous chapter an account was given of Railton's analysis of nitroglycerin in 1855, using Liebig's method for the determination of the relative quantities of carbon and nitrogen produced on combustion. The formula of nitroglycerin being taken as



the ratio of the volumes of carbon dioxide and nitrogen should be as 2 to 1. Railton obtained results varying from 2.156 to 1 down to 1.912 to 1. While these results were, on the whole, in favour of the above formula, they were not altogether satisfactory. Railton made no attempt to determine the carbon and hydrogen absolutely, as he found it impossible to dry his nitroglycerin, even in an exhausted receiver, on account of its great tendency to decompose. This proves that his sample was impure, as pure nitroglycerin is perfectly stable *in vacuo*.

In 1871, Beckerhinn,¹ who was engaged in a research on the action of ozone on nitroglycerin and gun cotton, published in the *Artillery Journal* of Vienna an analysis of nitroglycerin as follows:—

	Found.	Calculated for $\text{C}_3\text{H}_5(\text{NO}_3)_3$.
Carbon . .	15.42 15.62	15.85
Hydrogen . .	2.27 2.40	2.20
Nitrogen . .	— 17.90	18.50

Subsequent investigators, however, obtained rather widely varying results in their analyses of nitroglycerin.

Hess,² in 1874, gave the following figures as the result of his analysis of nitroglycerin by various methods:—

Method.	Nitrogen per cent.
Direct determination of N (Dumas) .	13.9, 14.1
N determined as NH_3 (Siewert) .	14.23
N „ NO (Schulze) .	13.7, 14.0

¹ *Mitt. über Gegenstände des Artillerie und Genie Wesen.* (1871), 42-54.

² *Zeit. f. anal. Chem.* (1874), 257.

He gives in addition the following results for nitroglycerin of various manufacture:—

Product.	N per cent.	Method of Manufacture.
Nobel's Zamky (1872)	14.0	Nobel's method
" (1873)	16.1	
Lithofracteur von Krebs	13.7	Krebs & Luckow
Dualin von Ditmar	13.9	Unknown
Rheinische Dynamit Fabrik	16.6	Mowbray's method
Opladen bei Köln		No air agitation

Sauer and Ador,¹ in 1877, determined by three methods the nitrogen in nitroglycerin extracted from dynamite. They first used Reichardt's modification of Schloesing's method (ferrous chloride and hydrochloric acid), after decomposing the liquid with potash, and obtained results from 12.3 to 14.0 per cent. of nitrogen. Next they tried ignition with soda-lime but found only 2.3 per cent. of the nitrogen evolved as ammonia. Finally they made four determinations by Dumas' method, from three different samples of dynamite, and obtained 18.35-18.52 per cent. of nitrogen, which agrees very closely with that calculated from the formula (18.5 per cent.).

Hess and Schwab,² in 1878, made some nitrogen determinations by Dumas' method. In one sample they found 15.72 and 15.65 per cent. of nitrogen, and in another (from Nobel's Zamky manufacture of 1872) they found 16.12 per cent. of nitrogen, though this was the same liquid which four years earlier had yielded Hess only 14.0 per cent. of nitrogen. It will be noted that there is a wide difference in the results obtained by these investigators for the percentage of nitrogen in nitroglycerin as determined by Dumas' method.

By far the most complete investigation, as regards the composition of nitroglycerin, was carried out by Hay and Orme Masson³ in 1887. All investigators, they say, agree in regarding this compound as a nitrate of glycerin, but while some considered it a trinitrate, others held that it was a mixture of tri, di and mononitrate. Previous analyses were quite insufficient to establish one or the other conclusion, and were mainly confined to the determination of nitrogen. As the decomposition of nitroglycerin by potash was shown by Hay to occur in a manner considerably different from that suggested by Railton, the main reason in support of the constitution of nitroglycerin

¹ *Berichte* (1877), 1982.

² *Berichte* (1878), XI., 192.

³ *Trans. Royal Soc. of Edinburgh* (1887), 87.

as a trinitrate was removed. The nitroglycerin employed by Hay and Masson was made by adding Price's pure glycerin (1 part) drop by drop to a mixture of nitric acid (2 $\frac{7}{8}$ parts) and sulphuric acid (6 parts), the mixture being surrounded by ice and kept at a temperature not exceeding 10° C. Five minutes were allowed to elapse before pouring the mixture into water, and the precipitated nitroglycerin was then washed eight times with large volumes of distilled water and dried for 7 hours in the air-bath at 70° C. It finally stood for 12 days over sulphuric acid in a vacuum desiccator. Not the slightest sign of decomposition ensued, and it was found that nitroglycerin after standing one week *in vacuo* had lost less than 0.1 per cent. in weight, which showed it was practically dry from the first. It was perfectly colourless and transparent and had a sp. gr. of 1.601 at 14.5° C. The carbon and hydrogen were determined by ignition in a tube closed and drawn out at one end, and filled with copper oxide and copper in the usual manner. At the termination of the ignition the drawn-out point was broken and a stream of oxygen passed. In the first experiment the nitroglycerin was weighed in a glass tube and dropped into the combustion tube; but an explosion occurred at an early stage of ignition, which, though damaging the furnace and injuring one of the experimenters, satisfied them that the explosive force of the quantity of material employed (0.23 grm.) was not so great as to prevent them continuing the experiments with the adoption of very ordinary precautions. It was ultimately found that the combustion could be performed without any risk of explosion as follows. Nitroglycerin (0.2-0.4 grm.) was weighed out in a porcelain boat containing finely-divided copper oxide and then covered with another layer. The boat was dropped into the combustion tube, and the contents well scraped out and mixed with granulated copper oxide. The chief difficulty arose from the introduction of moisture. The precautions were increased in each experiment, so that the last hydrogen determination is probably the most reliable. The same means were employed for filling the tube in the Dumas method for the determination of nitrogen. The following results were obtained:—

	Calculated.	I.	II.	III.	IV.	V.
C ₃	15.86	16.05	15.89	15.8	—	—
H ₅	2.20	2.99	2.40	2.08	—	—
N ₃	18.50	—	—	—	17.93	17.97
O ₉	63.44	—	—	—	—	—

Two nitrogen determinations were made with the same nitroglycerin before it was placed *in vacuo*. Results, 18.25 and 18.06 per cent. of nitrogen. The above figures, therefore, prove nitroglycerin to be glycerol trinitrate, the slight deficiency of nitrogen being probably due to traces of impurities (oxidized derivatives of glycerin) irremovable by the water with which the nitroglycerin was washed. The nitrogen was also determined in other samples of nitroglycerin prepared with different proportions of acid, to ascertain whether a difference in the method of preparation caused any corresponding difference in the composition of the liquid. The results show that this is not so. In these cases Dumas' method was not employed, but a modification of Schloesing's method which was found to give equally good results, in spite of the contrary experience of Hess and Schwab, and Sauer and Ador.

The weighed quantity of nitroglycerin was dissolved in absolute alcohol and decomposed by boiling for 10 minutes with excess of an alcoholic solution of caustic potash. Water was added and the whole of the alcohol driven off by evaporation; after which the fluid was made up to a given volume of which a measured portion was taken for the experiment. The volume of nitric oxide evolved by the reducing action of ferrous chloride and hydrochloric acid was in each case compared with the volume of gas obtained, under precisely the same conditions of temperature and pressure, from a standard solution of pure potassium nitrate and also from sodium nitrite. A correction is, however, necessary, since a small portion of nitrogen is always evolved as ammonia on boiling nitroglycerin with potash. The amount was determined in a preliminary experiment as follows. 1.1533 grms. of nitroglycerin were dissolved in 5 cc. of absolute alcohol and a solution of 1.5 grms. of caustic potash in absolute alcohol added, the flask being immediately connected with a modified Boussingault apparatus and then boiled. After half an hour an equal volume of water was added and the boiling continued three-quarters of an hour more. The distillate was titrated and found to contain 0.0053 gm. NH_3 which is equal to 0.38 per cent. of nitrogen lost as ammonia. This amount was therefore added in each case to the nitrogen found by Schloesing's method. The samples mentioned below were prepared under very varying conditions of acid composition,

etc., but the analyses show the products to be identical in composition:—

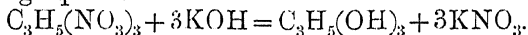
Sample.	N per cent. found.	N per cent. corrected for loss of NH_3 .
A	17.77	18.15
A	17.47	17.85
A	17.76	18.15
B	17.76	18.14
C	17.76	18.14
F	17.41	17.79
J	17.81	18.19
N	17.73	18.11
Nobel's	17.77	18.15

These figures agree closely, not only with each other, but with those obtained by the authors by Dumas' method. The analyses show it to be highly probable that nitroglycerin is invariable in composition, and that the statements of some previous investigators, particularly Hess, are erroneous. If nitroglycerin does, at any time, contain the lower nitrates, it is probably owing to very imperfect washing in the process of manufacture. Nitroglycerin is only very slightly soluble in water; glycerin is freely soluble; and, reasoning from the above analogy, it is highly probable that intermediate nitrates possess an intermediate solubility, which will readily permit of their removal by any ordinarily complete washing of the nitroglycerin with water, but may allow only of their partial removal if a limited quantity of water is used. According, however, to the published descriptions of various commercial processes for the manufacture of nitroglycerin, the washing appears to be sufficiently thorough to remove the lower nitrates, for the amount of washing necessary to remove traces of free acid used in the manufacture of nitroglycerin is certainly quite sufficient to dissolve out the lower nitrates.

CHAPTER XXVI

THE DECOMPOSITION OF NITROGLYCERIN BY CAUSTIC POTASH

THE action of a solution of caustic potash on nitroglycerin was represented, in 1855, by Railton¹ as occurring according to the following equation:—



It is rather a curious fact that, for some 32 years, Railton's equation was considered by chemists to be, in the main, correct, *i.e.*, that nitroglycerin was decomposed by a solution of potash with the production of potassium nitrate and the reformation of glycerin. It is true that some subsequent workers noticed the presence of nitrite, but it was apparently considered to exist in relatively a small proportion. All the workers appear to have accepted as a fact that there was a reformation of glycerin.

Muller and De la Rue² remarked upon the formation of nitrous acid in the spontaneous decomposition of nitroglycerin.

Beckerhinn,³ in 1876, carried out some work on the decomposition of nitroglycerin by an alcoholic solution of caustic potash, basing the interpretation of his results on Railton's formula. He added an excess of decinormal alcoholic potash to nitroglycerin, heated the mixture for 10 minutes at 60°-80° C., diluted with half the volume of water, added litmus, and titrated the excess of potash with a decinormal solution of oxalic acid. He quotes results showing nitroglycerin to contain 18.73 per cent. of nitrogen.

Hess and Schwab,⁴ in 1877, repeated Beckerhinn's work, but could not confirm his results. They noted that when nitroglycerin was treated with alcoholic potash, in the manner described by Beckerhinn, the liquid becomes yellow and rapidly deposits a yellow-brown precipitate. The solution, if diluted with only half its volume of water, was so strongly coloured that

¹ *Qr. J.C.S.* (1855), 7, 222.

² *Liebigs Ann.*, 109, 122.

³ *Sitzungs. Ber. Wien. Akad.* (1876), 73 [2], 235.

⁴ *Sitzungs. Ber. Wien. Akad.* (1877), 75 [2], 702.

it was impossible to titrate, with litmus as an indicator. They therefore diluted with four to five times the volume of water, but obtained results which showed from 25 to 26 per cent. of nitrogen. They further remarked that potassium nitrite is formed in addition to potassium nitrate, seeing that starch-iodide solution always gave a very strong colour, even in the most dilute solutions. Formic acid and acetic acid were also noted to be present, and in addition a brown body having properties very similar to aldehyde resin.

Matthew Hay,¹ in 1887, carried out a very complete investigation on this subject. Hay, in dealing with Railton's work, remarks that it is highly improbable that he obtained any glycerin at all, in decomposing nitroglycerin by caustic potash, as he probably mistook for glycerin a syrupy residue consisting of other substances. Hay's own work is of sufficient importance to be quoted at considerable length. When a moderately strong alcoholic solution of potash (1 in 10) is added to an alcoholic solution of nitroglycerin of similar strength, the following phenomena are observed. The first few drops produce an orange-coloured precipitate, which on the addition of more potash assumes, with the whole fluid, a deep reddish-brown colour. A large amount of heat is developed amounting almost to ebullition of the alcohol. A strong aldehyde odour is noticeable but no ammonia or acrolein. The fluid separates into two layers. The lower and smaller portion is partly of the nature of a solid precipitate, yet in a great part syrupy and of a very deep reddish-brown colour, and containing nearly all the colouring matter formed by the decomposition of the nitroglycerin. The upper layer constitutes the bulk of the fluid and is of a yellowish colour, first muddy and finally transparent. Heat is not necessary to complete the decomposition, but in most of the experiments the fluid was boiled over the water-bath for several minutes, sometimes to complete evaporation of the alcohol, water being added as the alcohol evaporated. When water is added, the syrupy precipitate, in proportion to the amount of alcohol still present, becomes partly or completely dissolved, yielding a deep red-brown solution. It was in such diluted solutions that determinations were made of the amount of potassium nitrite formed. This was effected by means of starch, potassium iodide and dilute sulphuric acid, a thoroughly

¹ *Trans. Roy. Soc. Edin.* (1887), 67.

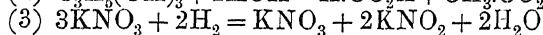
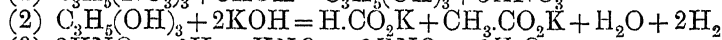
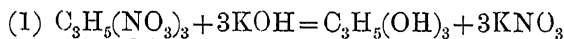
well-boiled 5 per cent. solution of starch, containing 2 per cent. of potassium iodide, being employed. The blue colour obtained on the addition of these reagents was compared, as regards its intensity, with the colour obtained by a standard sodium nitrite solution. The purity of the sodium nitrite was determined with permanganate, and the strengths were 1 in 500,000 and 1 in a million. The solution of decomposed nitroglycerin was diluted with distilled water until, on addition of the starch reagent, a depth of colour was obtained precisely similar to that given by the strongest solution of nitrite. The method was admitted to be only approximately correct, but it was the only one available. The following is an example of the method of analysis. Nitroglycerin (1.1533 grms.) was dissolved in 5 cc. of absolute alcohol and treated with 1.5 grms. of caustic potash dissolved in 12 cc. of alcohol. The mixture was boiled for half an hour, water being added to replace the evaporated alcohol, and the heating continued till the whole of the alcohol was driven off. The fluid was diluted to 30 cc. and 1 cc. was further diluted and employed for the determination of nitrous acid. A dilution corresponding to 1 of the original nitroglycerin in 620,000 of water was found to contain the same proportion of nitrous acid as the 1 in a million standard solution of sodium nitrite. The nitroglycerin had therefore produced a quantity of nitrous anhydride $\left(\frac{\text{N}_2\text{O}_3}{2}\right)$.

corresponding to 62 per cent. of the anhydride in sodium nitrite, or 34.143 per cent. of the nitroglycerin. The results obtained by this method from eight different samples of nitroglycerin, prepared under very varying conditions as regards composition of acids, etc., gave as an average approximately 35 per cent. of nitrous anhydride. Assuming that nitroglycerin is a trinitrate of glycerol, the results of these analyses correspond remarkably with the supposition that two out of the three parts of nitric anhydride are reduced to nitrous anhydride; for the trinitrate ought theoretically to yield, if so reduced, 33.48 per cent. The possibility of a nitrite group being present in nitroglycerin was negatived by the fact that two of the samples mentioned above, prepared in the presence of urea, were found to yield the same proportion of nitrous acid as the others. Other substances besides potassium nitrite are formed when alcoholic potash acts upon nitroglycerin. Potassium nitrate is present in considerable quantity, and there was reason to believe, from the total

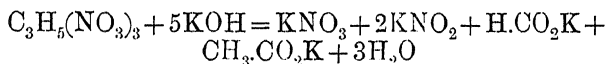
nitrogen, by Schloesing's method, and from other circumstances, that it corresponded closely to one-third of the nitrogen in nitroglycerin. The presence of potassium acetate and potassium oxalate was proved, and, doubtfully, of potassium formate. There was also a small amount of ammonia and a red-brown resinous body which gives a dark colour to the fluid. Finally, there was a very curious and interesting body which possessed the unusual power of forming a very firm jelly with a very large proportion of absolute alcohol. In contradiction to Railton and previous investigators, Hay found no glycerin, or only the merest trace. This was a new and most important fact. To ascertain the presence and nature of these various decomposition products, 6.67 grms. of nitroglycerin were decomposed with excess of potash. The fluid was allowed to stand for a day for the deposition of certain substances dissolved in the hot alcohol. The supernatant fluid, which was of a transparent orange colour, was decanted and the residue was boiled with alcohol, set aside, decanted and added to the previous fluid. The alcoholic fluid contained the excess of potash and the whole of the glycerin, if present. In the deep red-brown residue one would expect to find nearly all the colouring matter and the salts insoluble in alcohol, such as potassium nitrate and nitrite. The alcoholic fluid was neutralized with excess of sulphuric acid to precipitate potassium sulphate, and was then fractionally distilled to remove the more volatile substances (alcohol, acetic acid, formic acid), the less volatile glycerin remaining in the retort. The residue in the retort was saturated with barium hydroxide to remove the sulphuric acid, and the excess of barium was then precipitated by carbon dioxide. The filtrate evaporated on the water-bath gave 5 or 6 drops of a golden yellow viscid residue. When treated with absolute alcohol, in which glycerin is freely soluble, it hardened and was proved to consist of a barium salt. The alcoholic extract when evaporated yielded one drop of a yellowish syrup more viscid than glycerin and pungent rather than sweet, and gave only the faintest odour of acrolein when heated with acid potassium sulphate. The reddish-brown material when freed from potassium salts weighed 0.08 gm. and was of a resinoid character, probably similar to aldehyde resin or caramel.

Hay's work showed that Railton's equation was incorrect. When nitroglycerin is being decomposed by caustic

potash, nitric acid and glycerol occur in a very active and nascent condition, the one as a powerful oxidizing substance, the other as a readily oxidizable substance. As a consequence they act on each other, and two out of the three molecules of nitric acid part each with an atom of oxygen to the glycerol, and this amount of oxygen is sufficient to completely oxidize and break up glycerin, mostly, if not entirely, into certain organic acids, which, of course, will combine with the excess of alkali used for the decomposition. According to another view the caustic potash may be regarded as taking an active part in the decomposition of nascent glycerol, seeing that when glycerin is melted with caustic potash, potassium acetate and formate are produced along with free hydrogen. In accordance with these views the action of caustic potash on nitroglycerin may be represented as follows:—



or combining these equations—



The correctness of the equation is supported, as regards the amount of caustic potash, by the following. According to Railton's equation 1 part of nitroglycerin requires for complete decomposition 0.741 part of caustic potash. According to the equation just given the proportion is 1 to 1.235. If less caustic potash is used than in the latter proportion, then, if the latter equation be correct, complete decomposition will not occur, and a quantity of nitrous acid will be produced corresponding to the caustic potash employed, and the solution of the products of decomposition will remain neutral until more than the requisite proportion of caustic potash has been added. The following results prove this to be the case:—

Weight of Nitro- glycerin.	Weight of Potash.	Yield of Nitrous Anhydride as per cent. of Nitroglycerin.		Reaction.
		Calculated.	Found.	
1	0.8	21.68	23.23	Neutral
1	1.00	27.11	28.36	Neutral
1	1.24	33.48	34.69	v. slightly alk.
1	1.50	33.48	34.69	Alkaline.

CHAPTER XXVII

CERTAIN CHEMICAL DECOMPOSITIONS OF NITROGLYCERIN

REFERENCE has been made to Hay's¹ work on the decomposition of nitroglycerin by caustic potash. Hay also investigated the action of certain other chemical compounds, of which the following are the most important.

Action of Ammonia.—Similar action, but not so energetic as potash. With excess of ammonia no immediate decomposition takes place. The mixture remains colourless and no precipitate is formed. On boiling for an hour, and replacing the ammonia as it evaporates, the solution assumes an even deeper reddish-brown colour than is the case with caustic potash. The amount of nitrous anhydride formed was equal to 34.5 per cent. of the nitroglycerin used, and was exactly similar to the proportion obtained by means of fixed alkali. The ammonium nitrite formed would therefore appear to undergo but little decomposition under the conditions in which it is placed. This is probably due to the presence of free ammonia, the low heat employed, or perhaps highly concentrated alcohol hinders the decomposition of ammonium nitrite.

Action of Alkaline Carbonates.—The same reaction was observed with a yield of nitrous anhydride equivalent to 35.34 per cent. A 5 per cent. alcoholic solution of nitroglycerin, when boiled with an excess of potassium carbonate, is completely decomposed in an hour.

Action of Sodium Phosphate.—This salt was added in concentrated aqueous solution to a 1 per cent. alcoholic solution of nitroglycerin. After three or four minutes' heating, decomposition began, and the tint of the solution gradually deepened to an orange-red. At the end of 1½ hours' heating, 13.5 per cent. of nitrous anhydride was obtained in the solution, and it was observed on diluting with water that a considerable amount of nitroglycerin was precipitated. Sodium phosphate appears,

¹ *Trans. Roy. Soc. Edin.* (1887), 69.

therefore, to act upon nitroglycerin in much the same manner as the alkalis, only very much less powerfully.

Action of Sodium Chloride.—An excess of a concentrated solution of sodium chloride was mixed with a 1 per cent. alcoholic solution of nitroglycerin and heated for 35 minutes. No change of colour was observed, and the nitrous acid did not amount to more than a fraction of 1 per cent. Starch reagent yielded no blue colour with the fluid until sulphuric acid was added. There was, therefore, a trace of nitrous acid present as nitrite. The addition of caustic potash proved that sodium chloride had not decomposed the nitroglycerin.

Action of Hydrochloric Acid.—1.6 cc. of strong acid were diluted with 2 cc. of water and added to 10 cc. of a 1 per cent. alcoholic solution of nitroglycerin. After heating for half an hour, a trace of nitrous acid was found to be present. Half the volume of the fluid was heated with caustic potash and yielded 13.5 per cent. of nitrous anhydride. Hydrochloric acid had, therefore, decomposed 39 per cent. of the nitroglycerin, but whether with the formation of nitrous acid it was not possible to say. Hydrochloric acid in large excess decomposes nitroglycerin much more slowly than alkalis, and not much more quickly than sodium phosphate.

Action of Sulphuric Acid.—1.5 cc. of strong acid were diluted with 1 cc. of water, mixed with 10 cc. of a 1 per cent. alcoholic solution of nitroglycerin and heated for half an hour. The merest trace of nitrous anhydride was present in the fluid. One half of the fluid when treated with caustic potash yielded nitrous anhydride corresponding to 29.7 of the nitroglycerin. The sulphuric acid had, therefore, decomposed 11.3 per cent. of the nitroglycerin employed, and would appear to act less energetically than hydrochloric acid.

Action of Sulphuretted Hydrogen.—According to De Vrij, an ethereal solution of nitroglycerin is readily decomposed by sulphuretted hydrogen with copious precipitation of sulphur. Two 10 per cent. solutions of nitroglycerin were prepared, the one in alcohol, the other in ether. A rapid stream of sulphuretted hydrogen was passed for 15 minutes, and in the case of the alcoholic solution, for 15 minutes more at boiling point. Not the slightest trace of decomposition was observable. There was no change in colour, and a complete absence of sulphur, nitrous acid and decomposition products. Nitroglycerin was

abundantly precipitated from both solutions on the addition of water. De Vrij's experience was therefore due to using impure nitroglycerin.

Action of Alkaline Sulphides.—The reaction is very energetic. The mixture soon assumes a deep red-brown colour, the temperature rises, and the action of the sulphide is completed with a sudden and abundant precipitate of sulphur in every part of the mixture simultaneously. No gas is given off, and, contrary to expectation, after being boiled with the sulphide for half an hour, filtered to remove sulphur, treated with lead acetate, to remove sulphuretted hydrogen, and again filtered, it yielded evidence of the presence of nitrous acid to the extent of little less than one half the proportion yielded by purely alkaline decomposition. It would appear, therefore, that the whole of the nitrous anhydride set free is not acted upon by the sulphuretted hydrogen. For we may assume that the alkaline sulphide itself takes an initial step in the decomposition. The sulphuretted hydrogen plays a subsidiary part and merely acts on the nascent products of decomposition. It is difficult to explain, however, why the whole of the nascent nitrous anhydride should not thus be decomposed by sulphuretted hydrogen. It may be suggested that the nascent nitrous acid combines in part with the alkali, and, once so united, it is not capable of being acted on by sulphuretted hydrogen. But sulphuretted hydrogen does not play an altogether passive part in the actual decomposition of nitroglycerin itself, for when an aqueous solution of an alkaline sulphide is poured over pure undissolved nitroglycerin, and the mixture vigorously shaken, the solution becomes reddish, and when the temperature rises sufficiently, the whole of the nitroglycerin is suddenly decomposed with copious formation of sulphur. In fact the nitroglycerin seems to be converted into a mass of sulphur. When caustic potash alone acts on nitroglycerin, in such circumstances, the decomposition proceeds very slowly. The presence of sulphuretted hydrogen very greatly promotes the decomposition of nitroglycerin, but in what particular manner has not been definitely ascertained.

Action of Water.—A saturated aqueous solution of nitroglycerin was heated for 3 hours. There was no sign of decomposition, and no trace of nitrous acid, except when sulphuric acid was added, when a distinct blue coloration was obtained.

The nitrous acid had therefore combined with some other decomposition product of nitroglycerin, and was found to amount to 1.7 per cent. of the nitroglycerin employed. Potash treatment gave 8.88 per cent. of nitrous acid. Hence 73.48 per cent. of the nitroglycerin had been decomposed by heating with water for 3 hours. A portion of this may, however, have been lost by simple evaporation, though this was to a certain extent avoided by heating in a long-necked flask.

Action of Alcohol.—A 1 per cent. alcoholic solution of nitroglycerin was heated for 1 hour, the alcohol being renewed as it evaporated. There was no change in colour and no nitrous acid could be detected, even when sulphuric acid was added with the usual reagents. A portion of the fluid was decomposed with potash and the nitrous anhydride was found to amount to 33.45 per cent., proving that the nitroglycerin had not been decomposed by heating with alcohol. From this it is evident that alcohol, when used as a menstruum in ascertaining the action of other substances on nitroglycerin, does not of itself aid in the decomposition.

Solubility of Nitroglycerin.—The following figures were ascertained for the solubility of 1 grm. of nitroglycerin in the respective solvents mentioned. Water, 800 cc.; absolute alcohol, 4 cc.; rectified spirit, 10 cc.; methyl alcohol, 1 cc.; methylated spirit, 4 cc.; amyl alcohol, 18 cc.; ether, chloroform, carbolic acid and glacial acetic acid, all proportions; benzol, 1 cc.; carbon disulphide, 120 cc..

Yield of Nitroglycerin.—The yield of nitroglycerin was determined as obtained under very varying conditions of acid mixture and the proportion of glycerin employed. Price's pure glycerin, dried for 6 hours at 120° C., was used. The acids used were each of two strengths—nitric acid of 1.422 sp. gr. and 1.494 sp. gr., sulphuric acid of 1.844 sp. gr. and fuming sulphuric acid of 1.984 sp. gr. The mixed acids were always placed in salt and ice and cooled below 0° C. In certain cases where urea was also used it was added to the nitric acid previous to mixing it with sulphuric acid. The temperature of nitration was never allowed to rise above 10° C. This mixture was poured into a large and measured volume of cold water. The precipitated nitroglycerin was collected, and in this slightly impure state was dried at 70° C. The weight of dried nitroglycerin, increased by the proportion known to be lost by solution in the

water into which it had been thrown (calculated from a solubility of 1 in 800), gave the total yield of nitroglycerin. The following table gives the results of these experiments:—

GRMS.					Yield of Nitro-glycerin per cent.
Glycerin.	Nitric Acid.		Sulphuric Acid.		
	1·422	1·494	1·844	1·984	
12·4	—	30	75	—	—
6·1	urea 1 grm.	15	30	—	—
10·4	30	urea 1 grm.	30	—	16·3
8·8	25	" 1·5 "	50	—	107·8
10·2	30	—	60	—	163·8
10·8	30	—	90	—	175·6
10·6	30	—	90	—	180·2
9·4	—	20	20	20	202·7
10·2	—	20	10	30	184·3
9·6	30	—	30	—	30·1
10·3	—	30	90	—	227·1
10·5	—	30	30	30	233·3
10·25	—	30	20	40	231·7
10·0	—	30	60	—	234·1

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